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14. ABSTRACT
The thermal shock behavior and thermal residual stresses were investigated for zirconium diboride-based ultra-high temperature ceramics. The research employed a combined experimental and finite element modeling approach to understand the factors that affected the magnitude and spatial extent of residual stresses. Then, engineered architectures were designed and fabricated to mitigate thermal stresses. This approach led to an improvement in thermal shock behavior. Whereas the strength of conventional SiC particulate reinforced zirconium diboride ceramics decreased by more than 30% after quenching from ~400°C, fibrous monolithic ceramics could be quenched from temperatures as high as 1400°C without degradation of strength. The study of residual stresses revealed that the magnitude of the tensile stresses in the zirconium diboride matrix was relatively insensitive to the size of the silicon carbide particulates, but the spacial extent of the stresses was strongly linked to particle size and shape. A combination of elevated temperature neutron diffraction and Raman spectroscopy were used to measure thermal stresses for validation of the models.

15. SUBJECT TERMS
ultra-high temperature ceramics, thermal properties, finite element modeling, residual stress

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EXECUTIVE SUMMARY

This report summarizes research performed as part of the project "Design of Ultra-High Temperature Ceramics for Improved Performance," which was funded by AFOSR grant FA9550-06-1-0125. The report describes the technical progress and lists all of the publications and presentations that stemmed from the project. The report also describes interactions between the project team and other researchers from around the world. In addition to the technical content, the appendices describe two related subjects. The first appendix is a trip report prepared after the principal investigators attended the Fifth China International Conference on Ceramics in 2007. This conference had significant participation from researchers from across China who were investigating ultra-high temperature ceramics. The final appendix describes and lists additional projects related to boride and carbide ceramics that were active during the performance of this project. This AFOSR project was part of a larger effort at the Missouri University of Science and Technology that has become one of the largest research groups in the world focused on these unique materials.

The goal of the project was to understand the influence of composition and structure on elevated temperature behavior of ZrB_2-based ultra-high temperature ceramics. A combined experimental and modeling approach was used to gain the maximum fundamental understanding from a minimum number of experiments. The technical focus areas for the project were: 1) adapting mechanical models to monolithic, particulate reinforced, and fibrous monolithic UHTCs; 2) fabricating compositions and structures for testing and model evaluation by hot pressing, reactive hot pressing, sintering, and/or co-extrusion followed by hot pressing; 3) characterizing thermomechanical properties and thermal shock behavior.

Significant technical progress was made in several areas. First, the thermal shock behavior was characterized for conventional SiC particulate reinforced ZrB_2 ceramics and then improved by engineering the meso-scale structure of a novel ZrB_2-SiC fibrous monolith. Whereas monolithic ZrB_2 and ZrB_2 reinforced by 30 vol% SiC particulates both lost strength after quenching to room temperature from ~400°C, the fibrous monolith architecture could withstand quenching from 1400°C without loss of strength. The improvement was due to crack propagation being isolated to only the cell boundary phase. Finite element modeling was used to calculate and understand how parameters such as SiC particle size and shape affected the distribution of residual thermal stresses. Models experimental results that larger SiC particles led to residual stresses that affected a greater volume of the surrounding ZrB_2 matrix, but that the magnitude of the residual stresses did not vary significantly with particle size. Elevated temperature neutron diffraction experiments were used to validate and confirm the models. Further investigations of the effect of SiC distribution on the residual stresses in ZrB_2-SiC ceramics continue utilizing Raman spectroscopy. This work included designing and fabricating unique spiral architectures that were specifically constructed to mitigate thermal stresses.

The primary results of this research are detailed in the technical publications that resulted from the thesis and dissertation research of the graduate students. A complete list of publications and abstracts of the student thesis and dissertation documents are included in this report.

OBJECTIVES

The goal of this project was to understand the influence of composition and structure on residual thermal stresses and thermal shock behavior of ZrB_2-based ultra-high temperature ceramics. A combined experimental and modeling approach was used to minimize the number of experiments while maximizing the scientific benefit. The main technical tasks of the project were: 1) adapting mechanical models to monolithic, particulate reinforced, and fibrous monolithic UHTCs; 2) fabricating compositions and structures for testing and model evaluation by hot pressing, reactive hot pressing, sintering, and/or co-extrusion followed by hot pressing; 3) characterizing thermomechanical properties and thermal shock behavior.

STATUS OF EFFORT

This program began on January 1, 2006 and ended in December 2008. Significant progress was made toward the research objectives. The program is expected to have lasting impacts in several areas. The main areas of technical progress highlighted in this report are: 1) improved thermal shock behavior; 2) modeling of thermal stresses; 3) design of composite architectures for improved thermal stress mitigation; 4) effect of carbon content on properties of sintered ZrB_2-SiC; 5) spark plasma sintering of ZrB_2 ceramics; and 6) Raman spectroscopy for measuring thermal stresses in ZrB_2-SiC UHTCs.

In addition to the technical progress, the project was an integral part of a larger effort focused on research related to ultra-high temperature ceramics at the Missouri University of Science and Technology. During the course of this project, Professors Hilmas and Fahrenholtz collaborated on UHTC research projects that were funded by the National Science Foundation, The U.S. Army Space and Missile Defense Command, the Air Force Research Laboratory, Advanced Ceramics Research, Inc., and Hy-Tech Research Corporation. Together, the projects supported up to nine graduate students and a research engineer, all working on various aspects of boride and carbide ceramics. The synergy among the projects was critical in establishing the reputation of the UHTC group at Missouri S&T as a worldwide leader in studying the processing, microstructures, properties, and performance of UHTCs.

ACCOMPLISHMENTS/NEW FINDINGS

Thermal Shock Behavior

Thermal shock testing and modeling have been conducted for ZrB_2-based conventional and fibrous monolithic materials. Measured thermal and mechanical properties were used to calculate the thermal shock parameters (R, R', R'', R''', and R'''') for conventional ZrB_2 and ZrB_2-30 vol.% SiC that were prepared by hot pressing commercially available powders. The thermal conductivities measured for ZrB_2 and ZrB_2-SiC were 53 W/m•K and 70 W/m•K, respectively. These values were significantly lower than those reported in previous studies. Evaluation of the electron and phonon contributions to thermal diffusivity/conductivity indicated that the lower values measured for the Missouri S&T materials may be the result of grain size effects.

Based on the measured thermal and mechanical properties, R thermal shock parameters were calculated for ZrB_2 (140°C) and ZrB_2-SiC (200°C) using Equation 2:

$$R = \frac{\sigma(1-\nu)}{E\alpha}\psi(\beta) \qquad (2)$$

where σ is strength, ν is Poisson's ratio, E is Young's modulus, α is coefficient of thermal expansion, and $\psi(\beta)$ is a stress reduction factor. In addition to the calculated values listed in Table 1, the thermal shock resistance of the two materials was also measured using water quench testing. As shown in Figure 1, the critical ΔT measured for both conventional materials was ~400°C. The stress reduction factor, which is a function of the Biot modulus β, is used to correlate the calculated behavior (assumes instantaneous heat transfer) to measured values, where heat transfer is not instantaneous. Comparing the measured R to the calculated values gives a stress reduction factor of 0.364 for ZrB_2. Assuming the same stress reduction factor for ZrB_2-SiC reduces the R to ~144°C, which is lower than the value of 200°C predicted for ZrB_2-SiC. The lower value of the refined R compared to the calculated value may be due to microcracking induced by the thermal expansion mismatch at ZrB_2-SiC interfaces. Measured critical ΔT values were further supported by analysis that employed finite element modeling (FEM) to calculate temperatures and stress distribution in quenched specimens.

In contrast to the behavior of the conventional materials, ZrB_2-based fibrous monoliths showed a dramatic improvement in thermal shock behavior. Remarkably, fibrous monoliths retained their room temperature strength for quench temperatures up to 1400°C (Figure 1). The improved performance was attributed to the crack deflecting ability of the FM architecture. Further investigation of the elastic properties of the ZrB_2-based FMs showed a steady decrease in Young's modulus as a function of quench temperature. The modulus decreased from ~450 GPa for as-prepared materials to ~200 GPa for specimens quenched from 1400°C. The decrease in modulus may be an indication of damage accumulation in the specimens as quench temperature increased. However, the retained strength indicated that the load-bearing cells (ZrB_2-SiC) remain pristine after quenching. Further FEM analysis is underway to understand the role of the FM architecture in the observed thermal shock behavior.

Table 1. Summary of thermal shock parameters for ZrB_2 and ZrB_2-SiC.

Property	ZrB_2	ZrB_2 – 30 vol% SiC
Calculated R(°C)	140	200
Measured R(°C)	~385	~395
Stress reduction factor	0.364 (calculated)	0.364 (assumed)
'Refined' R	140	144

Modeling of Thermal Stresses

The focus of the research during this past year was final development of a finite element model to predict residual thermal stresses in ZrB_2-SiC ceramics and the measurement of residual stress using diffraction methods. The model was developed using ABAQUS to evaluate the influence of particle size and shape on residual thermal stresses. The particle size model, as seen in Figure 2, considered two simple round SiC particles in a ZrB_2 matrix, one 300 μm in diameter and the other 2 μm in diameter. Initial analysis showed that the volume of material within the higher tensile stress zone was much greater for the material with larger SiC particle size. Based on the statistical nature of the strength of brittle materials, a larger volume of material under tensile stress should increase the probability of encountering a critical-sized flaw, which should decrease strength. More detailed analysis of the model was warranted by this initial finding.

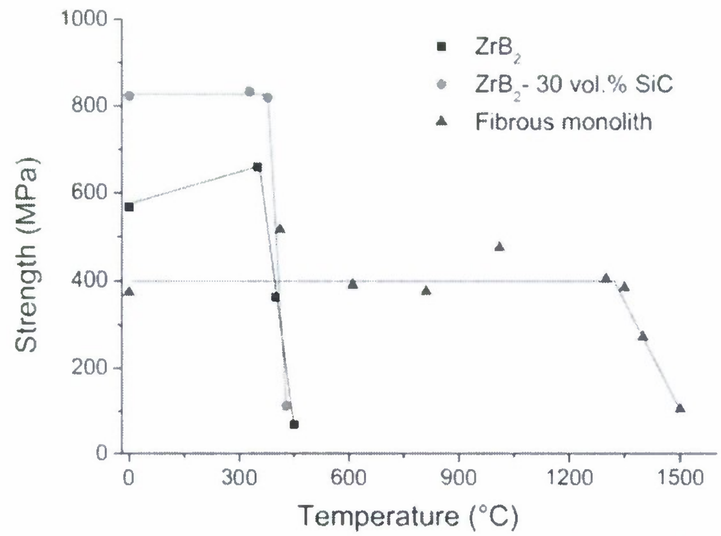

Figure 1. Experimental thermal shock behavior of conventional ZrB_2 and ZrB_2-SiC ceramics compared to ZrB_2-based fibrous monoliths.

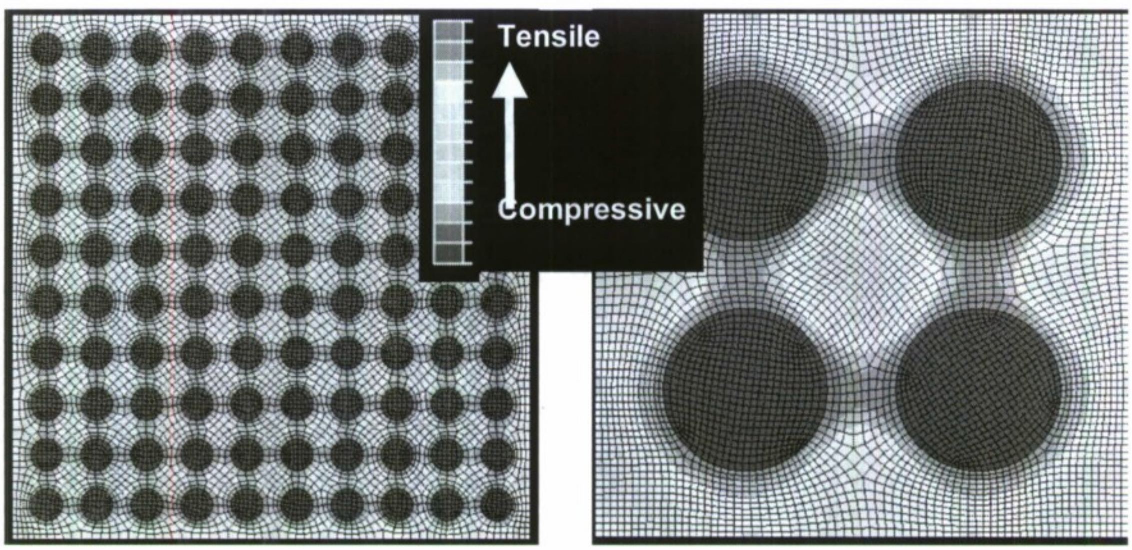

Figure 2. Output from an ABAQUS model of residual thermal stresses (tensile) in the ZrB_2 matrix around SiC particles of different sizes. Both materials contain 30 vol.% SiC.

Further analysis of the ABAQUS model evaluated the magnitude of the residual thermal stresses in both the ZrB_2 matrix and the SiC particles (Figure 3). The magnitude of the compressive stresses in the SiC particles only varied by ~100 MPa as the SiC particle size increased from ~1 μm to ~6 μm, remaining around 800 MPa. However, the maximum tensile stresses in the ZrB_2 matrix increase from ~1600 MPa for a SiC particle size of 1 μm to around 1775 MPa for a SiC particle size of 5 μm. The model results were then compared to strengths measured in previous experimental studies, which showed that the strength of ZrB_2-SiC decreased from ~1000 MPa when the SiC particle size was ~1 μm to ~400 MPa when the SiC particle size was ~6 μm. In addition to the change in the magnitude of the stresses, the volume of material affected by residual thermal stresses also increased with SiC particle size. The model results and experimental studies are consistent with the statistical nature of the strength of brittle materials since increasing the volume of material affected and increasing the magnitude of the residual stress should increase the probability of encountering a critical-sized flaw, which, in turn, should decrease the average strength.

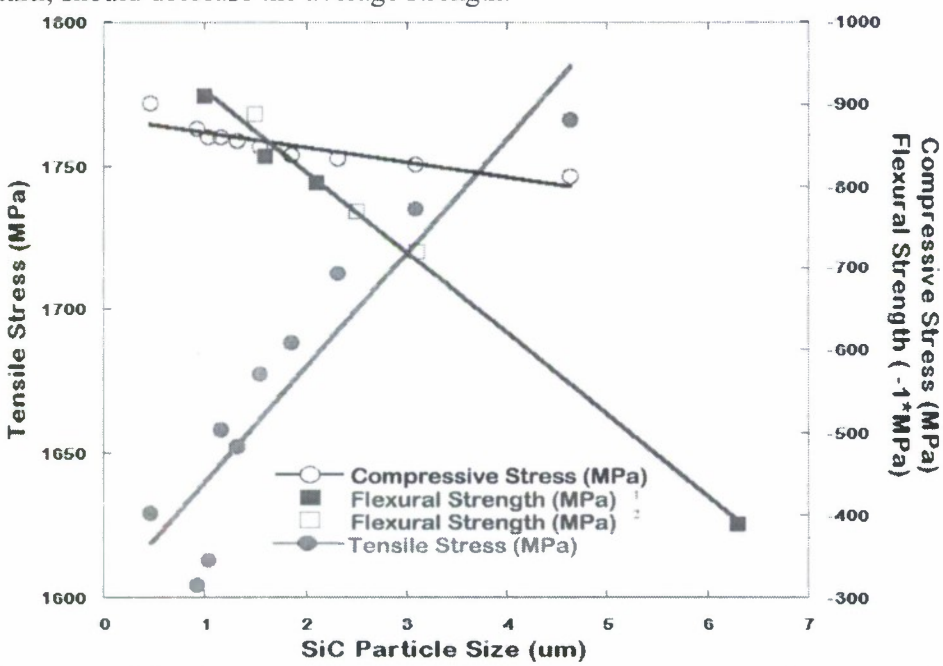

Figure 3. Model results showing the magnitudes of the predicted compressive stresses in SiC particles (open circles) and tensile stress in the ZrB_2 matrix (closed circles) in ZrB_2-SiC ceramics as a function of SiC particle size compared to flexural strengths measured experimentally in two studies (open squares[1] and closed squares[2]).

In an effort to validate the thermal stresses predicted by the model, neutron diffraction was employed to measure the residual thermal stresses in ZrB_2-SiC ceramics. Variable temperature neutron diffraction was selected as the primary characterization tool because of its

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1. A. Rezaie, W.G. Fahrenholtz, and G.E. Hilmas, "Effect of Hot Pressing Time and Temperature on the Microstructure and Mechanical Properties of ZrB_2-SiC," Journal of Materials Science, 42(8) 2735-2744 (2007)
2. S. Zhu, W.G. Fahrenholtz, and G.E. Hilmas, "Influence of Silicon Carbide Particle Size on the Microstructure and Mechanical Properties of Zirconium Diboride-Silicon Carbide Ceramics," Journal of the European Ceramic Society, 27(4) 2077-2083 (2007).

ability to sample a large volume of material due to the depth of penetration into the ceramic. Although high temperature x-ray diffraction could be used, the depth of penetration of the x-rays would limit the measurement to the first few micrometers of material below the surface. Neutron diffraction should be able to evaluate the residual stresses in the bulk ceramic. In the neutron diffraction experiment, the magnitude of the thermal residual stresses was measured as a function of temperature. In addition, the temperature at which the residual stresses were completely relaxed was also determined. However, the neutron absorption of boron was a potential impediment to this analysis.

Naturally occurring boron is a mixture of about 20% ^{10}B and 80% ^{11}B isotopes and has a high neutron absorption (768 Barns) due to the high absorption of the ^{10}B isotope (3837 Barns). Thus, ZrB_2 containing the normal distribution of isotopes does not work well with neutron diffraction. However, the ^{11}B isotope is nearly transparent to neutrons with an absorption of 0.0005 Barns. Thus, to minimize absorption during the neutron diffraction study, ZrB_2 parts were fabricated using isotopically pure ^{11}B. The purified ^{11}B was mixed with ZrH_2 to produce low absorption ZrB_2. First the ^{11}B starting particle size was reduced from greater than 10μm to around 1μm using ball milling. Then, isotopically pure $Zr^{11}B_2$ and $Zr^{11}B_2$-SiC were prepared by reactive hot pressing. The microstructure of the resulting ceramics was comparable to other ZrB_2-SiC materials (Figure 4). The mechanical properties of the resulting ceramics are summarized in Table 2. The strength, modulus, and hardness of the $Zr^{11}B_2$-SiC were all lower than that of the other material prepared by reactive hot pressing, probably due to the retention of a small volume fraction of porosity in the $Zr^{11}B_2$ material.

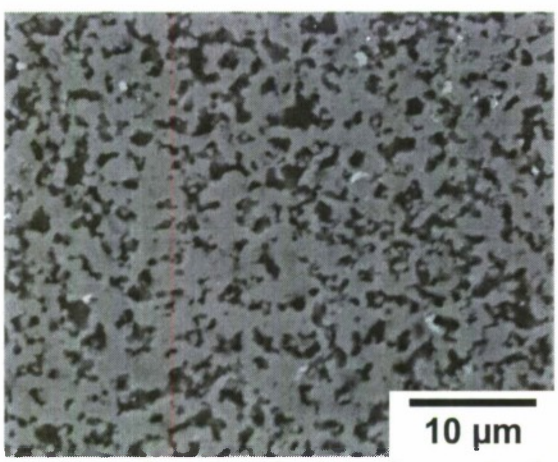

Figure 4. Scanning electron micrograph of a ZrB_2-SiC ceramic containing 30 vol.% SiC that was fabricated by reactive hot pressing using isotopically pure ^{11}B

Table 2. Summary of mechanical properties of ZrB_2-SiC[3] and isotopically pure $Zr^{11}B_2$-SiC, both prepared by reactive hot pressing (RHP).

	Strength (MPa)	Hardness (GPa)	Elastic Modulus (GPa)
ZrB_2-SiC	800 ± 115	27 ± 2	510
$Zr^{11}B_2$-SiC	373 ± 110	21 ± 1	412

3. A.L. Chamberlain, W.G. Fahrenholtz and G.E. Hilmas, "Low Temperature Hot Pressing of Zirconium Diboride Ceramics by Reactive Hot Pressing," Journal of the American Ceramic Society, 89(12) 3638-3645 (2006).

Neutron diffraction experiments were conducted at the Intense Pulsed Neutron Source (IPNS) at Argonne National Laboratory. Samples were loaded into the General Purpose Powder Diffractometer (GPPD) housed inside a molybdenum furnace. Diffraction data were collected in temperature increments of 50°C or 100°C from room temperature (25°C) to 1200°C. Analysis is ongoing to separate the effects of thermal expansion and residual stress from the data and to analyze a stress free reference sample. Figure 5 summarizes the peak positions as a function of temperature and Figure 6 shows an example diffraction pattern. The analysis showed that ^{11}B allowed for collection of meaningful neutron diffraction data from boron-containing ceramics. Currently, supplemental high temperature x-ray diffraction is being analyzed to evaluate the residual thermal stresses and thermal expansion behavior of ZrB_2 and SiC powders, which are presumably stress free since the individual particles are not constrained in a dense ceramic matrix, to allow for calculation of residual thermal stresses in the composite material. These data will also be analyzed to quantify the coefficient of thermal expansion for these materials.

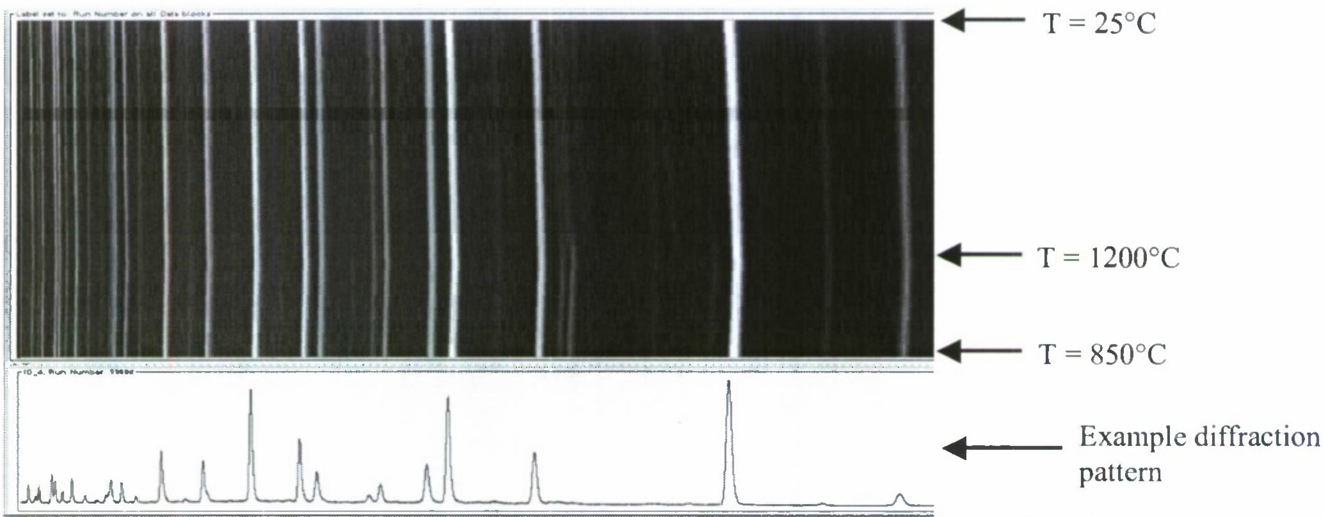

Figure 5. Peak positions as a function of temperature for the neutron diffraction study of $Zr^{11}B_2$-SiC. From the top of the plot, the lattice parameters increase as temperature increases from room temperature (25°C) to a maximum of 1200°C and then the lattice parameters decrease as temperature drops to 850°C. A room temperature diffraction pattern is shown on the bottom of the plot.

Design of Composite Architectures for Mitigating Thermal Stresses

Computer modeling results suggested that spiral shaped SiC inclusions would reduce the magnitude of the residual thermal stresses in the ZrB_2 matrix (Figure 7). Co-extrusion processing was used to fabricate spiral shaped SiC inclusions in a ZrB_2 matrix. For this process, SiC and ZrB_2 were separately dispersed in thermoplastic binders. Sheets of the polymer blends were rolled and compacted to produce a one inch diameter composite feed rod (Figure 8a). The feed rod was then extruded to reduce the diameter of the spiral to ~300 µm (Figure 8b). The spiral architecture was preserved through the size reduction process. After chopping the extruded filament into ~500 µm lengths, the filaments were mixed with ZrB_2 powder and hot pressed for densification.

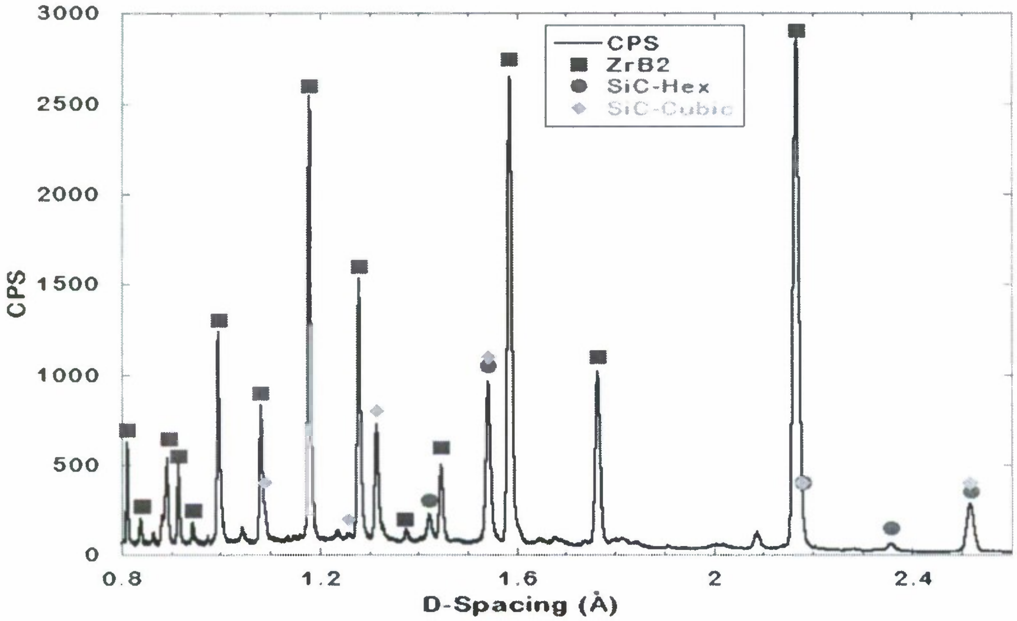

Figure 6. Neutron diffraction pattern for $Zr^{11}B_2$-SiC at room temperature.

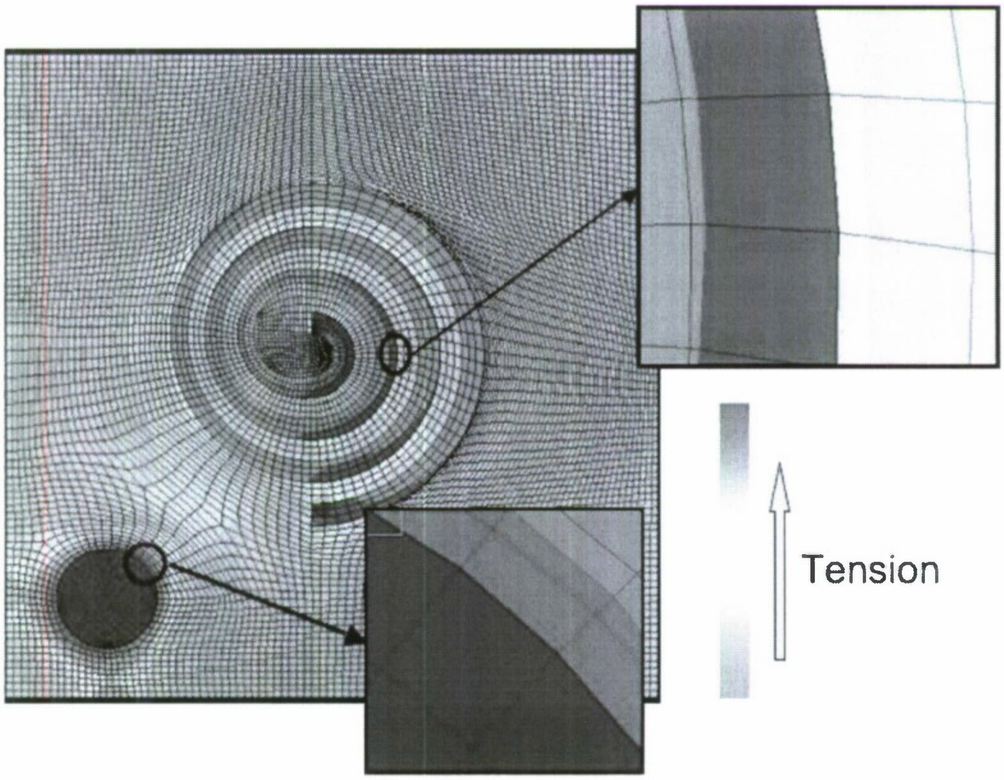

Figure 7. Finite element model of the residual thermal stresses in the ZrB_2 matrix in the vicinity of a round SiC inclusion and a spiral shaped SiC inclusion showing the magnitude of the stresses was lower around the spiral.

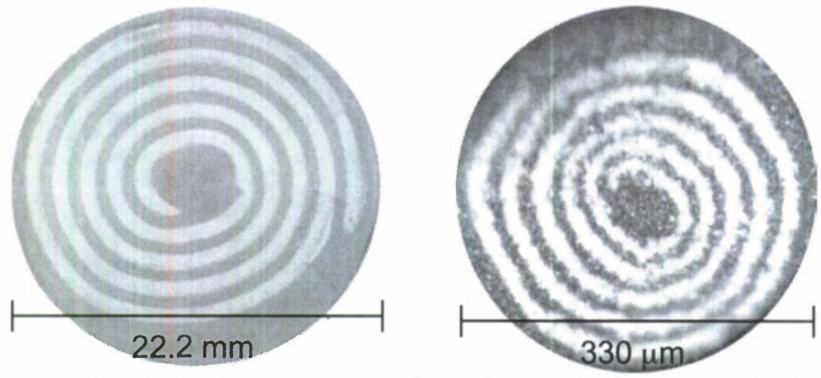

Figure 8. Optical micrographs of (a) a ZrB_2-SiC feed rod and (b) extruded filament for fabrication of spiral shaped reinforcements in ZrB_2-SiC.

Ceramics composed of 70 vol.% ZrB_2 reinforced with 30 vol.% of SiC in the form of spiral-shaped inclusions were densified by hot pressing. Analysis of the microstructure (Figure 9) showed that the spiral architecture was maintained through densification and that the spirals were distributed in different orientations in the matrix. Mechanical testing (Figure 10) of the spiral reinforced material revealed that the material had a low average strength (~150 MPa), which can be attributed to the size of the SiC inclusions. As stated earlier in the report, the SiC particle size was the critical factor that determined the strength of ZrB_2-SiC ceramics. The measured strength indicated that the critical flaw size in the spiral reinforced materials was likely to be more than 10 µm, which could correspond to the thickness of one of the layers in the spiral or some other feature. In addition to the strength testing, Vickers' indentations were used to qualitatively assess the damage tolerance of the ceramics. As shown in Figure 11, cracks induced by indentations in the ZrB_2 matrix were deflected by the layers of SiC in the spirals. Based on the strength and indentation testing, the spiral-reinforced ZrB_2 ceramics show promise as materials with improved damage tolerance compared to standard particulate reinforced ceramics without the need for the addition of expensive high strength fibers. Further analysis is underway to fully understand the mechanical behavior of these materials.

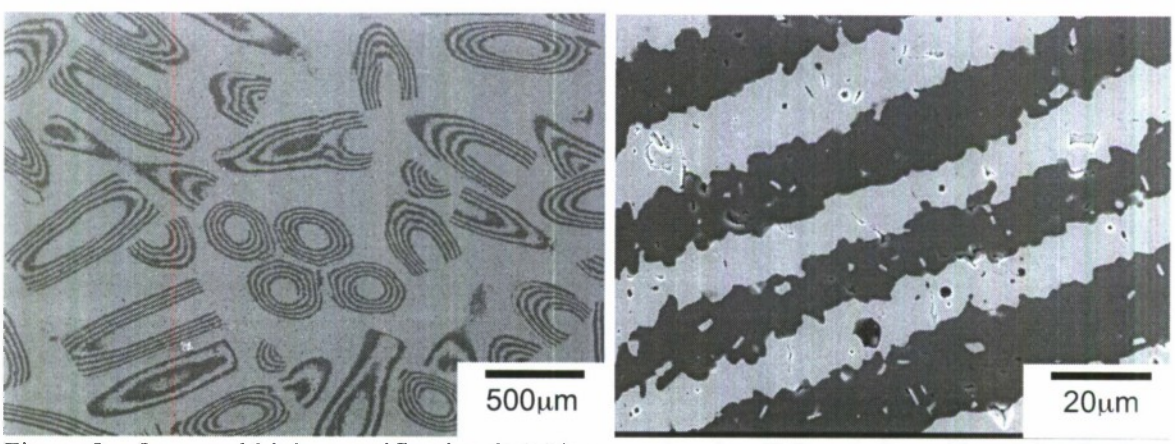

Figure 9. Low and high magnification SEM images showing ZrB_2 reinforced by ~30 vol.% spiral-shaped SiC inclusions. The low magnification image shows that the spirals have varied orientations. The high magnification image shows that the SiC is nearly fully dense and the ZrB_2 has a low volume fraction of porosity.

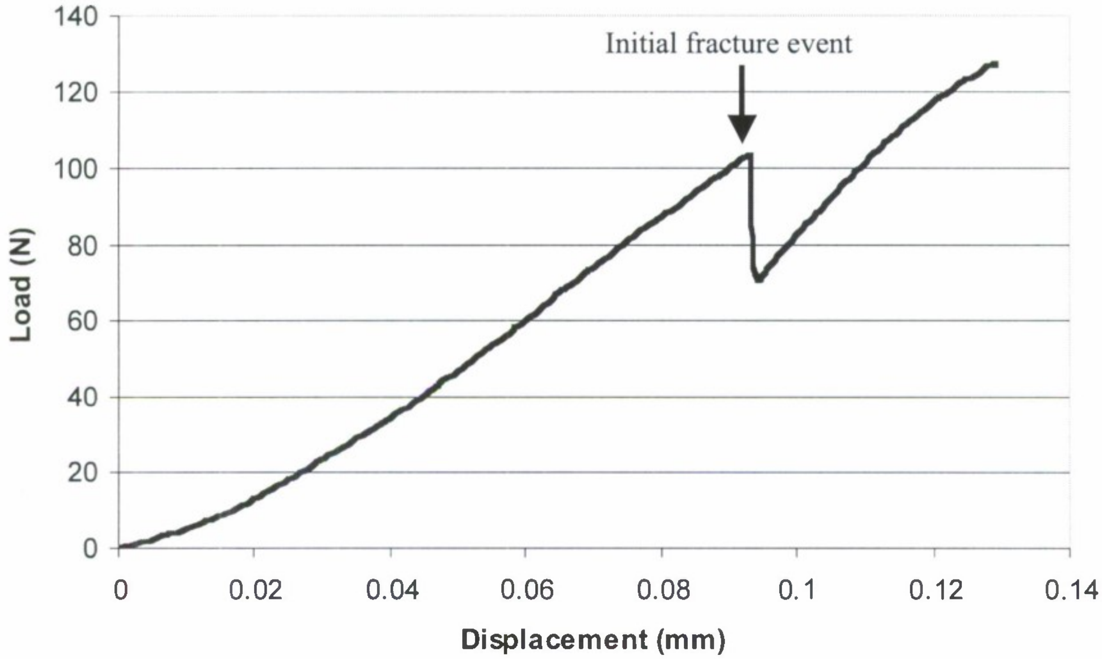

Figure 10. Load displacement curve for a flexure test of ZrB_2 reinforced with spiral-shaped SiC inclusions showing significant load retention after an initial fracture event.

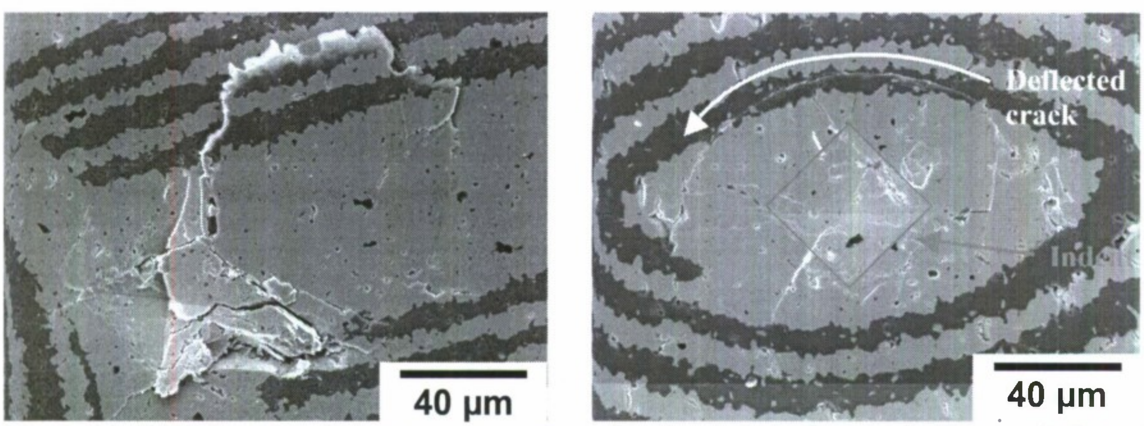

Figure 11. SEM images of Vickers indentations showing indentation cracks that are deflected by the SiC layers in the spirals.

Effect of Carbon Content on Properties of Sintered ZrB_2-SiC

The effect of carbon additions on the pressureless sintering behavior of ZrB_2-SiC ceramics was investigated. Previous research[4] has shown that carbon is an effective densification aid for ZrB_2-SiC due to its ability to react with and remove surface oxide impurities

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4. S.C. Zhang, G. Hilmas, and W.G. Fahrenholtz, "Pressureless Sintering of ZrB_2-SiC Ceramics," Journal of the American Ceramic Society, 91(1) 26-32 (2008).

associated with both ZrB_2 (i.e., ZrO_2 and B_2O_3) and SiC (i.e., SiO_2). As part of the present study, carbon additions ranging up to ~5 wt% were used to promote densification during pressureless sintering. Figure 12 shows bulk and relative density as a function of carbon additions for ZrB_2 ceramics containing 30 volume percent SiC that were pressurelessly sintered at 2050°C. Bulk and relative density were highest for carbon additions in the range of 2.6 wt% to 3.0 wt%. Lower carbon additions may not have been sufficient to remove enough oxide to allow for densification. The decrease in bulk density above 3.0 wt% carbon may be due to the presence of excess carbon in these materials. The microhardness (Figure 13) exhibits the same trends as density, presumably for the same reasons.

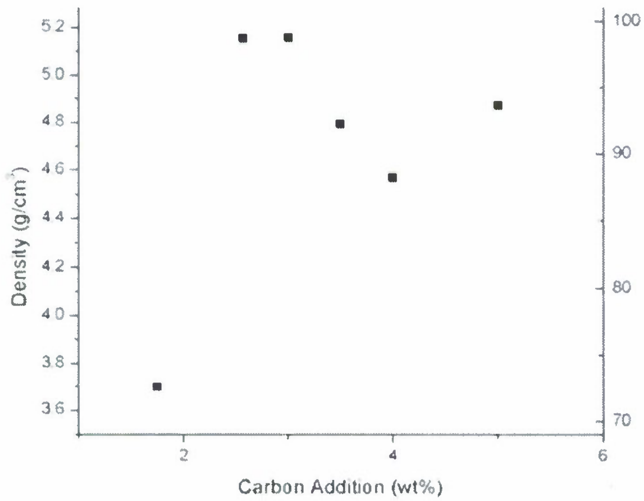

Figure 12. Bulk and relative density of pressurelessly sintered ZrB_2 containing 30 vol% SiC as a function of carbon addition.

Analysis of microstructure by SEM shows that ZrB_2-SiC containing less than 2 wt% carbon did not sinter to full density at 2050°C (Figure 14a). Large, connected porosity was present in the specimen containing 1.8 wt% carbon. In contrast, full density was reached for carbon contents above ~2.6 wt% (Figure 14b). Note that no carbon was observed in the microstructure of ceramics with carbon additions between 2.6 and 3.0 wt%, indicating that the carbon was removed by reaction with oxide surface impurities and/or dissolution into the matrix. It is likely that both occurred as carbon has a reported solutiliby of ~2 at% in ZrB_2. At higher carbon contents, above ~3.0 wt%, carbon was observed in sintered ZrB_2-SiC (Figure 15). At these levels, enough excess carbon was present to not only react with the oxide surface impurities, but also to saturate the ZrB_2. Both density and carbon content had an impact on the mechanical properties of the resulting ceramics. For ZrB_2-SiC with 2.6 wt% carbon added, the apparent elastic modulus was 435 GPa. The modulus decreased due to porosity for lower carbon contents (E = 227 GPa for 1.8 wt% carbon when relative density was ~75%) and due to the presence of carbon at higher carbon contents (E = 151 GPa for 3.5 wt% carbon added when relative density was ~93%).

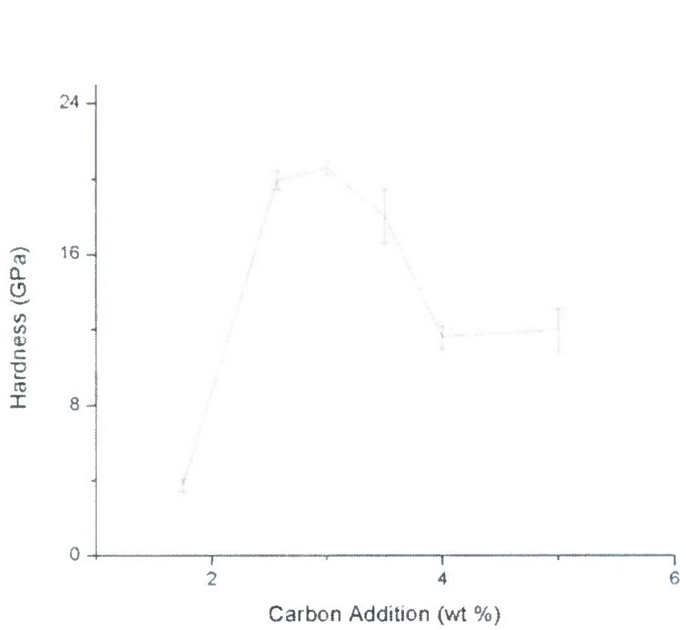

Figure 13. Hardness as a function of carbon additions in pressurelessly sintered ZrB_2 containing 30 vol% SiC.

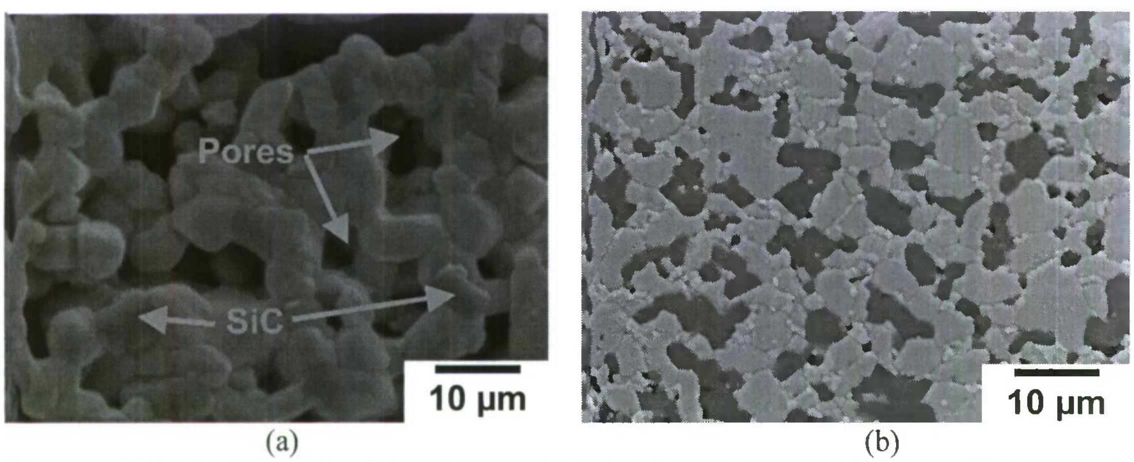

Figure 14. SEM images of polished, thermally etched cross sections of ZrB_2 containing 30 vol% SiC that was pressurelessly sintered at 2050°C containing (a) 1.8 wt% carbon and (b) 2.6 wt% carbon as a densification aid.

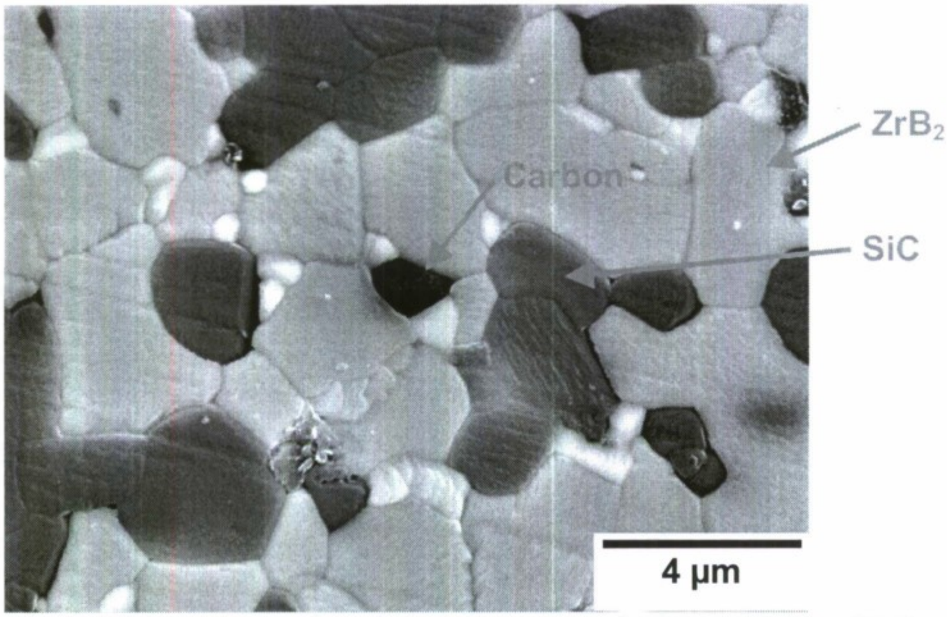

Figure 15. SEM image of a polished, thermally etched cross section of ZrB_2 containing 30 vol% SiC that was pressurelessly sintered at 2050°C containing 3.5 wt% carbon as a densification aid. Note the carbon inclusion in the microstructure.

Spark Plasma Sintering of ZrB_2 Ceramics

The densification behavior of ZrB_2 was studied with the goal of understanding the influence of starting particle size, oxygen content, and densification method on the development of microstructure and properties. The starting particle size was varied by using ZrB_2 with two different starting particle sizes (4 µm or 2 µm). Some materials were prepared by further reducing the particle size by attrition milling some of the powders. Oxygen content was varied by either increasing the surface area of the particle by attrition milling, by adding carbon to react with and remove some of the oxygen impurities, or by partially oxidizing the particles by heat treatment in air. Finally, the densification methods were conventional hot pressing (HP), pressureless sintering (PS), and spark plasma sintering (SPS). Information on the starting powders, oxygen contents, particle sizes and sample designations is summarized in Table 3. The oxygen contents were values that were measured prior to densification.

Each of the types of powders were densified by each of the sintering methods. A plot of the relative density as a function of densification temperature is shown in Figure 16. In general, relative density increased as temperature increased for each of the different starting powders. For hot pressing, each of the materials reached full density at 1900°C. For pressureless sintering, only the powder that was attrition milled and had carbon added (AMC) reached high relative density under the conditions studied. After sintering at 1900°C, compacts of AMC reached ~95% density. Due to limited availability of the equipment, fewer conditions were studied for SPS. Using SPS, densities of >95% were achieved for both AMO and AMC at temperatures of 1900°C or 2000°C.

Table 3. Sample designations, particle sizes, and oxygen contents of the materials for the densification study.

Designation	Powder (H.C. Starck)	Particle Size (microns)	Oxygen content (wt%)
ARC	As received ZrB_2 (Grade A) with 1 wt% carbon	~4	0.8
AM	Attrition milled ZrB_2 (Grade B)	0.2	2.1
AMC	Attrition milled ZrB_2 (Grade B) with 3 wt% carbon	0.2	2.1
AMO	Attrition milled ZrB_2 (Grade B) oxidized at 500°C for 10 min	0.2	8.2

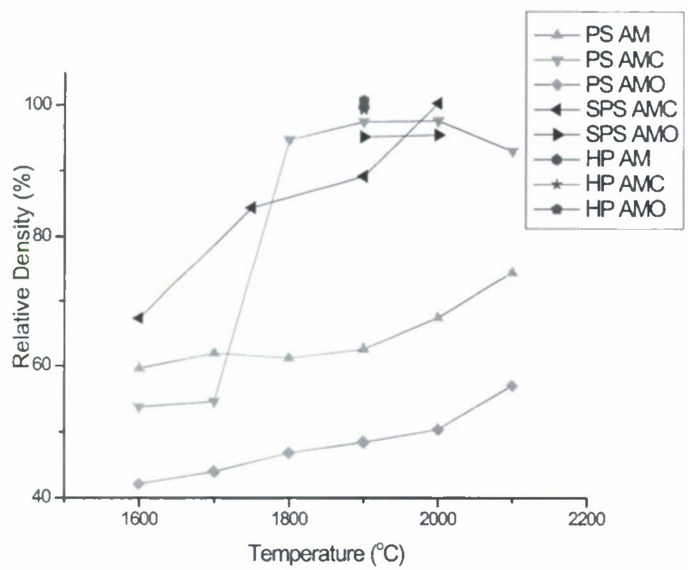

Figure 16. Relative density as a function of temperature for selected ZrB_2 powders using different sintering methods (PS, HP, SPS).

The results of the initial densification study were analyzed to select specimens with a range of grain sizes for a study of mechanical properties (Table 4). The measured bulk densities were converted to relative density by dividing by the true density of ZrB_2, which was assumed to be 6.09 g/cm^3. The calculated relative densities varied from ~86% for SPS ARC to over 100% for HP AMC and SPS AMC, although most were >95%. Relative densities greater than 100% were due to the incorporation of an unknown amount of WC into the batches during the attrition milling, which resulted in an underestimation of the true density and overestimation of the relative density in the initial density calculations. Likewise, the relative density of specimens with carbon contents above ~3 wt% may be underestimated since the effect of excess carbon was not accounted for in the density calculation. Further analysis of microstructures by SEM (Figures 17-19) revealed that most of the materials appeared to have high relative density as almost no porosity was observed on polished, thermally etched surfaces. In contrast, the SPS AMO specimen had a significant volume fraction of porosity.

Table 4. **Summary of density and mechanical properties of ZrB_2 ceramics.**

	Bulk Density (g/cm^3)	**Relative density based on pure ZrB_2 (%)**	**Average grain size (µm)**	**Failure strength (MPa)**	**Elastic modulus (GPa)**
PS AMC	5.90	96.8	31.8 ± 4.8	160 ± 20	393 ± 85
HP AM	6.07	99.6	3.1 ± 1.7	471 ± 105	523 ± 19
HP AMC	6.24	102.4	3.3 ± 1.5	460 ± 76	505 ± 26
SPS ARC	5.25	86.1	7.1 ± 2.3	445 ± 40	405 ± 21
SPS AMC	6.29	103.2	4.1 ± 1.6	527 ± 68	493 ± 20
SPS AMO	5.81	95.4	7.3 ± 2.1	431 ± 41	421 ± 20

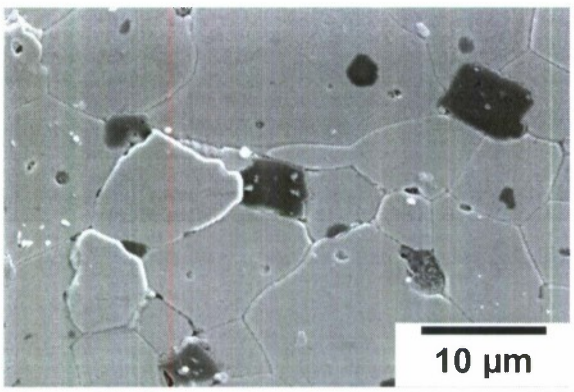

Figure 17. Representative microstructure of ZrB_2 densified by pressureless sintering (PS AMC).

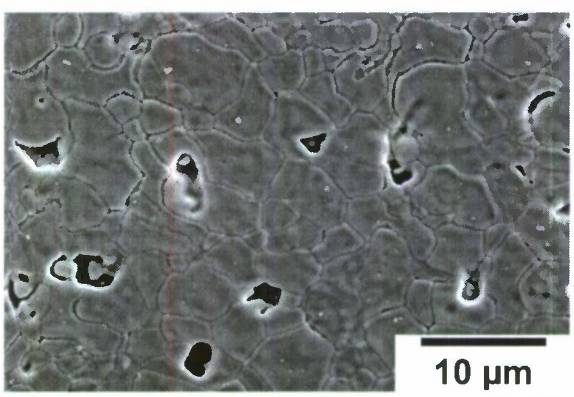

Figure 18. Representative microstructure of ZrB_2 densified by hot pressing (HP AMC).

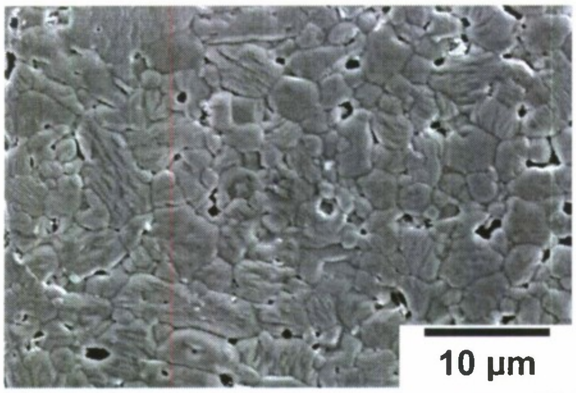

Figure 19. Representative microstructure of ZrB_2 densified by SPS (SPS AMC).

The room temperature mechanical behavior of the ceramics was further analyzed by plotting strength as a function of inverse square root of grain size (Figure 20). In general, strength increased as grain size decreased, independent of other factors such as starting particle size. The trend for the ceramics densified by pressureless sintering and hot pressing is shown as a dashed gray line in Figure 20. However, the strengths of ceramics densified by spark plasma sintering were higher than expected based on grain size. Because all of the ceramics had high relative density, porosity is not expected to be a contributing factor. SPS AMC had an average strength of 527 MPa and a grain size of 4.1 µm. Despite having a finer grain size of 3.3 µm, HP AMC had a lower strength (460 MPa). The two materials had similar elastic moduli (both ~500 GPa) indicating that neither residual porosity nor excess carbon were significant in either material. From the observation that densification by SPS leads to increased strength than expected based on grain size alone, it appears that SPS alters some other characteristic about the ceramics that impacts room temperature strength. Research is continuing to determine if the increased strength of the SPS material is due to chemical (e.g., grain boundary chemistry or change in impurity concentrations) or physical (e.g., residual stress) effects.

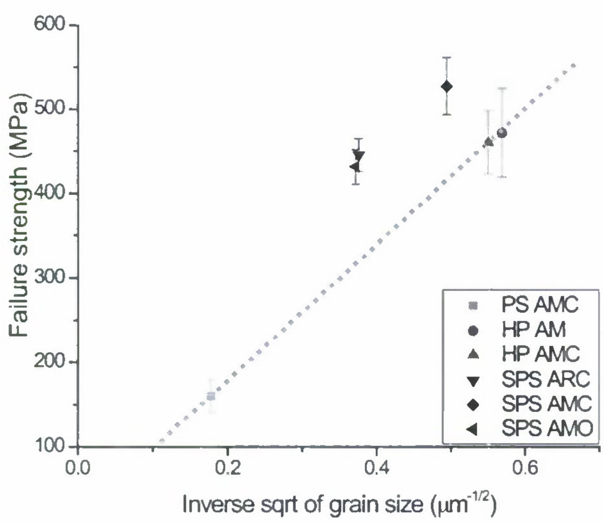

Figure 20. Strength as a function of inverse square root of grain size (Hall-Petch relationship) showing that densification by SPS results in higher strength compared to the strength-grain size trend of the other materials (dashed gray line).

Residual Stress Measurements and Model Validation

The relationship between SiC particle size and strength of ZrB_2-SiC ceramics was investigated using a combined experimental and modeling approach. The modeling was discussed in the section titled "Modeling of Thermal Stresses." For the experimental portion of the study, which is reported in this section, ZrB_2-SiC ceramics were prepared with SiC particle sizes ranging from ~1.5 μm up to as large as ~13 μm (Table 5). The strength of the resulting ceramics was tested to expand understanding of structure-property relations in the ZrB_2-SiC system and to provide specimens for direct measurement of residual stresses using neutron diffraction and Raman spectroscopy. The measured thermal stresses will be used to determine the temperature for the relaxation of thermal stresses, which is needed to finalize the thermal stress models.

Table 5. Summary of the maximum and average SiC particle sizes and strength of ZrB_2-SiC ceramics prepared using SiC powders with different starting particle sizes.

Composition	Max Particle size (μm)	Average Particle Size (μm)	Strength (MPa)
UF-25	3	1.6	1150 ± 115
UF-10	4.5	2	924 ± 00
UF-5	5.5	2.8	892 ± 120
Milled 12 hr	6	2.7	825 ± 118
Milled 4 hr	7	4	724 ± 83
Unmilled	13	8	245 ± 23

Previous studies have shown that smaller particle sizes of SiC lead to higher ultimate strength, as would be expected based on analysis using a Griffith flaw size approach as discussed in the papers of Rezaie et al. and Zhu et al. described in the FEM section. Plotting strength as a function of the maximum size of SiC particles observed in the ceramics shows a linear relationship (Figure 21). Finite element modeling discussed above revealed that larger particles reduced strength due to an increase in the volume of ZrB_2 under residual tensile stress (i.e., thermal stress) due to the thermal expansion mismatch between the SiC inclusions and the ZrB_2 particles. The stresses developed as the ceramics were cooled from the processing temperature (typically 1900°C), through the temperature where the thermal stresses are locked into the microstructure (neither known nor able to be predicted from using FEM), to room temperature.

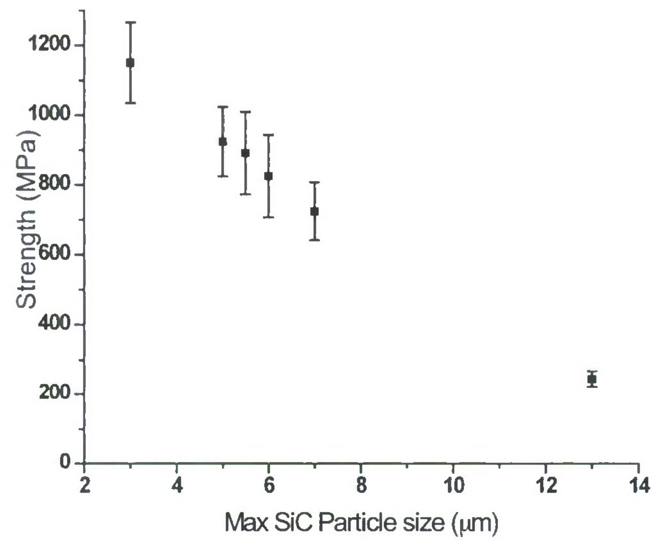

Figure 21. Strength as a function of the maximum size of SiC particles observed in ZrB_2-SiC ceramics.

Using the ceramics described in Table 5, Raman spectroscopy was employed to measure the residual compressive stress in the SiC particles generated during cooling from the processing temperature. The peak positions in Raman spectroscopy are sensitive to stress (Figure 22). Zirconium diboride is not Raman active, so the stresses in the matrix cannot be calculated directly. However, SiC is Raman active, so measuring the SiC peak positions for the different ceramics can be used to determine the residual thermal stresses in SiC particles at room temperature Relationships established by Liu and Vohra[5] can be used to calculate the compressive stress in the SiC particles from Raman spectra (Table 6). The finite element model can then be used to calculate the residual tensile stresses in the ZrB_2 matrix.

Table 6. Summary of residual compressive stresses measured in SiC using Raman spectroscopy and the corresponding tensile stresses predicted for the ZrB_2 matrix in ZrB_2-SiC ceramics.

Composition	Measured Compressive Stress in SiC (MPa)	Calculated Tensile Stress in ZrB_2 (MPa)
UF-25	870	970
UF-10	870	967
UF-5	800	890
Milled 12 hr	800	890
Milled 4 hr	700	780
Unmilled	700	780

5. J. Liu and Y. K. Vohra, "Raman Modes of 6H Polytype of Silicon Carbide to Ultrahigh Pressures: A Comparison with Silicon and Diamond," *Physical Review Letters*, **72[26]** 4105.1994.

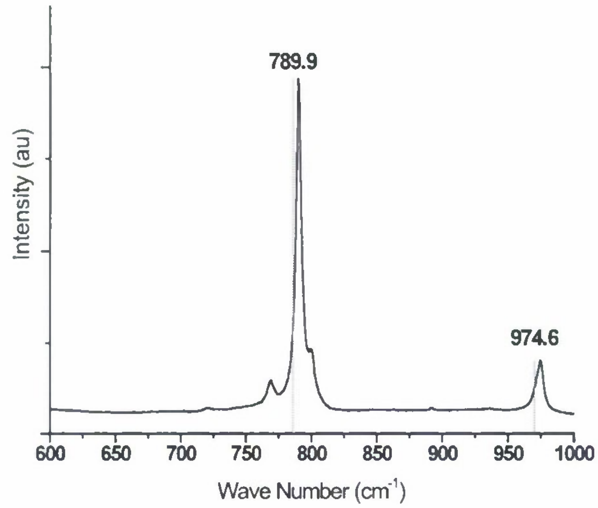

Figure 22. Raman spectrum for a ZrB_2-SiC ceramic showing shifting of the SiC peaks to higher wave number, indicating a residual compressive stress.

Residual stresses were also measured using the Spectrometer for Materials Research at Temperature and Stress (SMARTS) at Los Alamos National Laboratory. The SMARTS facility was used to collect diffraction patterns for ceramic and powder specimens during heating from room temperature to 1750°C and then during cooling from 1750°C back to room temperature. In turn, the diffraction patterns were analyzed to calculate the lattice parameters. Comparing the position of the SiC (006) peak between a SiC powder sample and a dense ZrB_2-SiC ceramic revealed that the SiC in the composite developed a compressive stress upon cooling as indicated by its smaller lattice parameter (Figure 23). A residual compressive stress of ~650 MPa was calculated for the SiC. The lattice parameters of powder sample and composite start to deviate below about 1200 °C during cooling. This indicates that the temperature at which stresses begin to accumulate upon cooling occurs around 1200°C.

The residual stress measurements from the neutron diffraction data were used to set the "zero stress temperature" in the FEM analysis. For the FEM, it as assumed that the residual stresses could relax at elevated temperature and only began to build when the temperature was below 1200°C, based on the neutron diffraction data. The stresses predicted by FEM were then compared to those measured calculated from the Raman spectra (Figure 24). Although not an exact fit, the predicted and measured stresses show the same trends and similar magnitudes. For example, the FEM analysis predicted a residual compressive stress of ~825 MPa for a SiC particle size of 3 μm compared to a compressive stress of ~870 MPa calculated from Raman peak shifts for the same particle size.

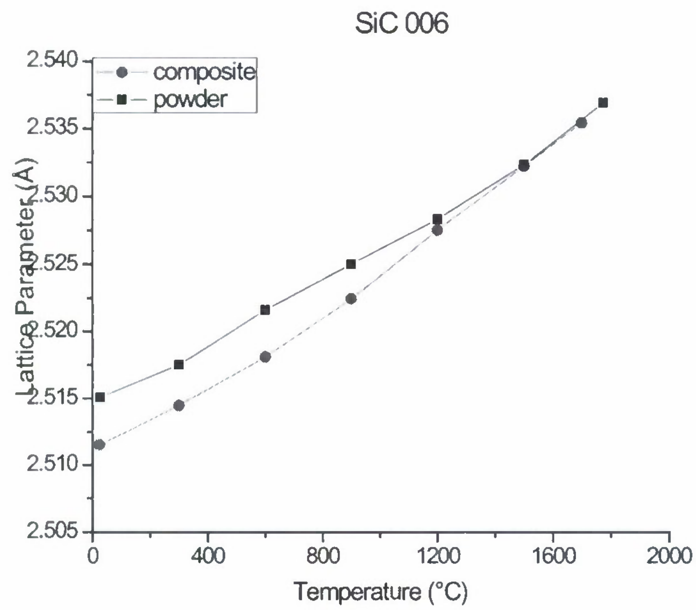

Figure 23. Lattice parameters as a function of temperature as determined for the (006) SiC peak as a powder sample and a ceramic were cooled from 1500°C to room temperature.

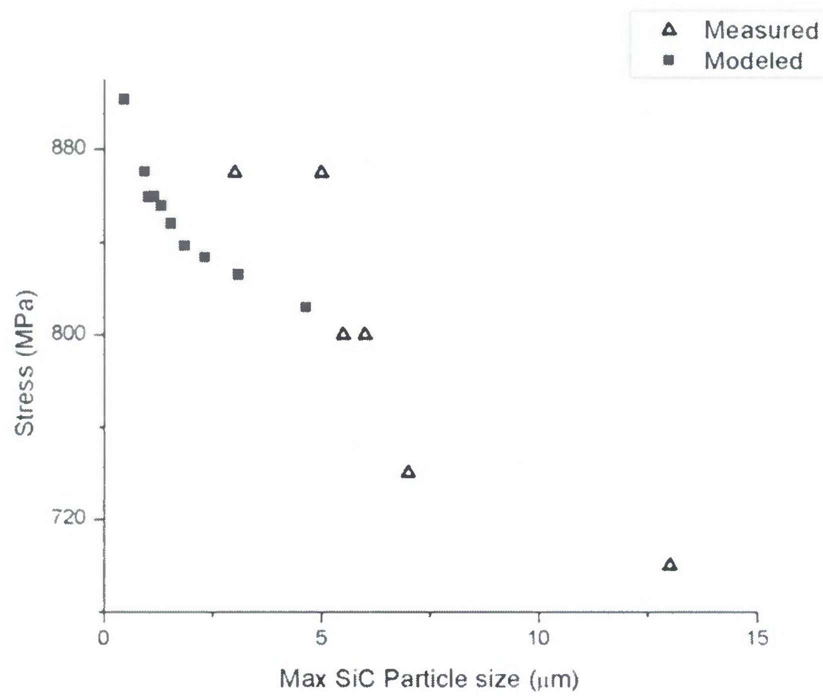

Figure 24. Comparison of predicted and measured compressive stresses in SiC particles in ZrB_2-SiC ceramics after cooling to room temperature. The FEM model assumed that thc residual stresses started to develop at ~1200°C.

PERSONNEL SUPPORTED

Table 7. Personnel supported or associated on AFOSR contract FA9550-06-1-0125.

Name	Title/Role	Level of Support
Dr. Bill Fahrenholtz	Co-PI	1 mo. summer salary
Dr. Greg Hilmas	Co-PI	1 mo. summer salary
Jim Zimmermann	Grad. research assistant, co-extrusion	50% time GRA
Michael Teague	Grad. Research assistant, modeling	50% time GRA
Adam Chamberlain	Grad. fellow, reactive hot pressing	50% time GRA
Jeremy Watts	Grad. Research assistant, residual stress	50% time GRA
Matt Thompson	Grad. Research assistant, properties	50% time GRA
Lindsey Campbell	Undergraduate, hot pressing	Part time in 2006
Taylor Woehl	Undergraduate, powder processing	Part time in 2007
Trevor Williams	Undergraduate, hot pressing	Part time in 2007
Jonathan Bock	Undergraduate, sample prep, testing	Part time in 2008
Eric Neumann	Undergraduate, testing and characterization	Part time in 2008

PUBLICATIONS AND PRESENTATIONS

Peer-Reviewed Journal Publications

1. J. Marschall, D.A. Pejakovi, W.G. Fahrenholtz, G.E. Hilmas, S. Zhu, J. Ridge, D.G. Fletcher, C.O. Asma, O. Chazot, and J. Thömel, "Oxidation of ZrB_2-SiC Ultra-High Temperature Ceramic Composites in Dissociated Air," accepted for publication in Journal of Thermophysics and Heat Transfer, January 2009.
2. M. Playez, D.G. Fletcher, J. Marschall, W.G. Fahrenholtz, G.E. Hilmas, and S. Zhu, "Optical Emission Spectroscopy During Plasmatron Testing of ZrB_2-SiC Ultra-High Temperature Ceramic Composites," accepted for publication in Journal of Thermophysics and Heat Transfer, January 2009.
3. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Thermal Shock Resistance of ZrB_2 and ZrB_2-30% SiC, Materials Chemistry and Physics, 112(1) 140-145 (2008).
4. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, R. Dinwiddie, W. Porter, and H. Wang, "Thermophysical Properties of ZrB_2-Based Ceramics," Journal of the American Ceramic Society, 91(5) 1405-1411 (2008).
5. W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, and S. Zhu, "Pressureless Sintering of Zirconium Diboride: Particle Size and Additive Effects," Journal of the American Ceramic Society, 91(5) 1398-1404 (2008).
6. W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, and J.A. Zaykoski, "Refractory Diborides of Zirconium and Hafnium," Journal of the American Ceramic Society, 90(5) 1347-1364 (2007).
7. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, F. Monteverde, and A. Bellosi, "Fabrication and Properties of Reactively Hot Pressed ZrB_2-SiC Ceramics," Journal of the European Ceramic Society, 27(7) 2729-2736 (2007).

8. W.G. Fahrenholtz, "Thermodynamic Analysis of ZrB_2-SiC Oxidation: Formation of a SiC-Depleted Region," Journal of the American Ceramic Society, 90(1) 143-148 (2007).

Peer-Reviewed Conference Proceedings

1. G.E. Hilmas and W.G. Fahrenholtz, "Ultra-High Temperature Ceramics for Applications in Extreme Environments," published in "Global Roadmap for Ceramics – Proceedings of the Second International Ceramics Congress," ed. by N. Babini and A. Bellosi, June 29-July 4, 2008, Verona, Italy.
2. M.P. Teague. G.E. Hilmas, and W.G. Fahrenholtz, "Finite Element Modeling of Internal Stress Factors for ZrB_2-SiC Ceramics," accepted for publication in the 32nd Annual International Conference on Advanced Ceramics and Composites, January 27-February 1, 2008, Daytona Beach, FL.

Theses and Dissertations

1. J.W. Zimmermann, "Improving the Thermal Shock Resistance of Zirconium Diboride Ceramics," Ph.D. Dissertation, University of Missouri-Rolla, 2007.
2. M.P. Teague, "Modeling and Measurement of Thermal Residual Stresses and Isotope Effects on Thermophysical Properties of ZrB_2-SiC Ceramics," M.S. Thesis, Missouri University of Science and Technology, May 2008.

Invited Presentations

1. G.E. Hilmas and W.G. Fahrenholtz, "Structure-Property Relations in Monlithic and Functionally Engineered ZrB_2-Based Composites," Ultra-High Temperature Ceramics: Materials for Extreme Environment Applications, Lake Tahoe, NV, August 3-8, 2008.
2. G.E. Hilmas and W.G. Fahrenholtz, "Ultra-High Temperature Ceramics for Applications in Extreme Environments," The Second International Ceramics Congress, June 29-July 4, 2008, Verona, Italy.
3. G.E. Hilmas and W.G. Fahrenholtz, "Structure-Property Relations in Monolithic and Fibrous Monolithic ZrB_2-Based Ceramics," Materials Science and Technology Conference and Exhibit, September 16-20, 2007, Detroit, MI.
4. W.G. Fahrenholtz, "Sintering of ZrB_2," Gordon Research Conference on Solid State Studies in Ceramics, August 5-10, 2007, Andover, NH.
5. W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, and S. Zhu, "Processing Challenges Related to Oxide Impurities in Boride-Based UHTCs," AFOSR Workshop on Ultra-High Temperature Ceramics," July 23-25, 2007, Menlo Park, CA.
6. G.E. Hilmas, W.G. Fahrenholtz, and J.W. Zimmermann, "Improving the Thermal Shock Resistance of ZrB_2-Based UHTCs," AFOSR Workshop on Ultra-High Temperature Ceramics," July 23-25, 2007, Menlo Park, CA.
7. W.G. Fahrenholtz and G.E. Hilmas, "Reactive Processing and Oxidation of ZrB_2-Based Ceramics," Fifth China International Conference on High-Performance Ceramics, Changsha, China, May 10-13, 2007.
8. G.E. Hilmas and W.G. Fahrenholtz, "Structure-Property Relations in Monolithic and Fibrous Monolithic ZrB_2-Based Ceramics," Fifth China International Conference on High-Performance Ceramics, Changsha, China, May 10-13, 2007.

9. W.G. Fahrenholtz and G.E. Hilmas, "Ultra-High Temperature Ceramics Research at the University of Missouri-Rolla," Chinese Academy of Sciences-Shanghai Institute of Ceramics, May 8, 2007, Shanghai, China.

Conference Presentations

1. J. Zimmermann, P. Marudhachalam, G. Hilmas, B. Fahrenholtz, A. Bellosi, F. Monteverde, "Properties of Intermetallic Ceramics with High Temperature Capabilities," AIAA Region I Young Professional and Student Conference - 2008, November 21-22, 2008, Baltimore, MD.
2. J. Watts, M. Teague, G. Hilmas, and W. Fahrenholtz, "Micro Raman Stress Measurements in ZrB_2/SiC Composites Having Particulate and Engineered SiC Additions," Materials Science and Technology Conference and Exhibition, October 5-9, 2008, Pittsburgh, PA.
3. M.J. Thompson, W.G. Fahrenholtz, G.E. Hilmas, and S.C. Zhang, "Effect of Carbon Content on the Strength of Pressurelessly Sintered Zirconium Diboride – Silicon Carbide Ceramics," Materials Science and Technology Conference and Exhibition, October 5-9, 2008, Pittsburgh, PA.
4. M.J. Thompson, W.G. Fahrenholtz, and G.E. Hilmas, "Effect of Oxygen Impurity Content on the Microstructure and Properties of Zirconium Diboride," Materials Science and Technology Conference and Exhibition, October 5-9, 2008, Pittsburgh, PA.
5. M.P. Teague, J.L. Watts, G.E. Hilmas, and W.G. Fahrenholtz, "Impact of Boron Isotope on the Thermal Properties of ZrB_2-SiC Ceramics," Materials Science and Technology Conference and Exhibition, October 5-9, 2008, Pittsburgh, PA.
6. M.P. Teague, G.E. Hilmas, and W.G. Fahrenholtz, "Finite Element Modeling and Neutron Diffraction Testing of Residual Thermal Stresses in ZrB_2-SiC Ceramics," 32nd Annual International Conference of Advanced Ceramics and Composites, January 28-February 1, 2008, Daytona Beach, FL.
7. J. Watts, M.P. Teague, G.E. Hilmas, and W.G. Fahrenholtz, "Modeling, Processing, and Properties of ZrB_2-Based Ceramics with Engineered SiC Architectures," 32nd Annual International Conference of Advanced Ceramics and Composites, January 28-February 1, 2008, Daytona Beach, FL.
8. M.P. Teague, G.E. Hilmas, and W.G. Fahrenholtz, "Finite Element Modeling and Neutron Diffraction Testing of Residual Thermal Stresses in ZrB_2-SiC Ceramics," Materials Science and Technology Conference and Exhibit, September 16-20, 2007, Detroit, MI.
9. J. Watts, M. Teague, G. Hilmas, and W. Fahrenholtz, "Modeling, Processing, and Properties of ZrB_2 Ceramics with Novel SiC Additions," Materials Science and Technology Conference and Exhibit, September 16-20, 2007, Detroit, MI.
10. M.P. Teague, G.E. Hilmas, and W.G. Fahrenholtz, "Finite Element Modeling of Internal Stresses in ZrB_2-SiC Ceramics," 31st Annual International Conference of Advanced Ceramics and Composites, January 21-26, 2007, Daytona Beach, FL.
11. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Thermal Shock of ZrB_2-Based Fibrous Monoliths," 31st Annual International Conference of Advanced Ceramics and Composites, January 21-26, 2007, Daytona Beach, FL.

12. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Reactive Processing of ZrB_2 and ZrB_2-SiC Ceramics," 31st Annual International Conference of Advanced Ceramics and Composites, January 21-26, 2007, Daytona Beach, FL.
13. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, A. Bellosi, and F. Monteverde, "Mechanical Properties of ZrB_2-25 vol.% SiC Fabricated Using Three Different Methods," Materials Science and Technology (MS&T) 2006, October 15-19, 2006, Cincinnati, OH.
14. J.W. Zimmermann, W.G. Fahrenholtz, and G.E. Hilmas, "Experimental Thermal Shock Properties of ZrB_2-Based Materials," Materials Science and Technology (MS&T) 2006, October 15-19, 2006, Cincinnati, OH.
15. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, F. Monteverde, and A. Bellosi, "ZrB_2-25 vol.% SiC Fabricated In-Situ by Reactive Hot Pressing of ZrH_2, B_4C, and Si," Materials Science and Technology (MS&T) 2006, October 15-19, 2006, Cincinnati, OH.
16. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Low Temperature Processing of Zirconium Diboride Ceramics," Materials Science and Technology (MS&T) 2006, October 15-19, 2006, Cincinnati, OH.
17. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz," Water Quench Thermal Shock Testing of ZrB_2-SiC," 30th Annual International Conference of Advanced Ceramics and Composites, January 22-26, 2006, Cocoa Beach, FL.
18. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Reactive Processing of Zirconium Diboride Ceramics," 30th Annual International Conference of Advanced Ceramics and Composites, January 22-26, 2006, Cocoa Beach, FL.

INTERACTIONS/TRANSITIONS

1. Graduate student Jim Zimmermann spent a semester working with Drs. Monteverde and Bellosi at the Institute for Science and Technology for Ceramics (ISTEC) in Faenza, Italy. Jim's work focused on processing ZrB_2-SiC and thermal shock testing. One jointly authored manuscript has been submitted that compares the properties of UHTCs fabricated by methods developed at ISTEC and UMR. Additional jointly authored manuscripts on high temperature mechanical behavior and thermal properties are being prepared.
2. The team collaborated with Dr. Joe Marschall from SRI International. We supplied ZrB_2-SiC disks to Dr. Marschall, which he submitted for arc heater testing at VKI in Belgium. The results and subsequent analysis are detailed in two manuscripts that have been accepted for publication in the Journal of Thermophysics and Heat Transfer as listed above.
3. ZrB_2-SiC hot pressed by the UMR team was submitted to the Southern Research Institute for high temperature mechanical testing. Dr. Sam Causey was the point of contact.
4. The Missouri S&T research team has used the facilities at the High Temperature Materials Laboratory at Oak Ridge National Laboratory to measure the elevated temperature thermal properties of ZrB_2-based ceramics. Students Jim Zimmermann and Michael Teague have both submitted proposals and traveled to Oak Ridge to make measurements of thermal diffusivity, heat capacity, and thermal residual stresses.

5. Graduate student Jeremy Watts conducted elevated temperature stress measurements using neutron diffraction using the Spectrometer for Materials Research at Temperature and Stress (SMARTS) facility at the Los Alamos National Laboratory. The research was supervised Dr. Dan Brown with assistance from Dr. Bjorn Clausen and Thomas Siseros. At this time, the data have been collected, but analysis continues. Results and analysis will be included in future collaborative publications between Missouri S&T and LANL as well as the PhD dissertation of Jeremy Watts.
6. Based on advice from Dr. Dileep Singh, graduate research assistant Michael Teague applied to use the Intense Pulsed Neutron Source (IPNS) facility of Argonne National Laboratory. The general purpose powder diffractometer (GPPD) was used to collect neutron diffraction patterns from flexure bars of ZrB_2-SiC at temperatures up to 1200°C. Powder diffraction studies, which are required for calculation of residual stresses, have now been completed at LANL and will be reported in a subsequent publication based on Michael's M.S. thesis.
7. During 2008, graduate research assistant Matt Thompson worked with Dr. Mike Cinibulk at the Air Force Research Laboratory at Wright-Patterson Air Force Base to densify ZrB_2-based ceramics by spark plasma sintering. Matt traveled to AFRL, was trained to use the SPS unit, and allowed to prepare a series of specimens that have been described in a recent presentation. We expect to prepare a collaborative manuscript based on this research in 2009 that will become part of Matt's PhD dissertation. In addition, Mike Cinibulk will be considered for membership on Matt's PhD committee depending on the direction that the future research takes.

DISCOVERIES, INVENTIONS, AND PATENT DISCLOSURES

One patent disclosure has been filed based on the research supported by this project. A provisional patent application has been filed for the unique spiral architectures that were developed to mitigate thermal residual stresses in ZrB_2-SiC ceramics.

1. G.E. Hilmas, W.G. Fahrenholtz, and J. Watts, "A Method for Toughening Via the Production of Spiral Architectures Through Powder Loaded Polymeric Extrusion and Toughened Material Formed Thereby," U.S. Provisional Patent Application 60/972,493, filed September 14, 2007.

AWARDS

Awards for Dr. Fahrenholtz

1. Promoted to Full Professor effective September 1, 2008
2. Fellow of the American Ceramic Society, elected September 2007
3. Univ. of New Mexico School of Engineering Distinguished Young Alumnus, October 2006
4. Faculty Excellence Award, Missouri S&T, 2006, 2007, and 2008
5. Sustained Teaching Excellence, School of Mat'ls Energy and Earth Resources, UMR, 2007

Awards for Dr. Hilmas

1. Faculty Excellence Award, Missouri S&T for 2006, 2007, and 2008

2. Outstanding Teaching Award, Missouri S&T, 2005-2006 and 2006-2007
3. Sustained Teaching Excellence, School of Mat'ls Energy and Earth Resources, 2005, 2007
4. Tau Beta Pi, Missouri Beta Chapter - Outstanding Engineering Professor, 2006

Awards for Jeremy Watts

1. Chancellor's Fellowship, Missouri S&T, 2006-present

Awards for Matthew Thompson

1. Chancellor's Fellowship, Missouri S&T, 2007-present

APPENDIX A: SUMMARY OF TRIP TO CHINA

The Fifth China International Conference on High Performance Ceramics

A TRIP REPORT PREPARED FOR THE AIR FORCE OFFICE OF SCIENTIFIC RESEARCH

Bill Fahrenholtz and Greg Hilmas
University of Missouri-Rolla
Rolla, MO 65409

May 21, 2007

Overview

This report summarizes the technical content related to ultra-high temperature ceramics (UHTCs) at the Fifth China International Conference on High Performance Ceramics, which was held May 10-13, 2007. The conference venue was the Va Ya International Hotel in Changsha in the Hunan province of the People's Republic of China. The conference series started in 1997 in Beijing. This report describes the technical content of the conference, but also includes details of our interactions with other groups during the trip. The most significant of the other interactions were with the Shanghai Institute of Ceramics (SIC) and a group of researchers from the Institute for the Science and Technology of Ceramics (ISTEC) in Faenza, Italy who joined us for the tour of SIC.

Trip Overview

The group from the University of Missouri-Rolla (UMR) included Bill Fahrenholtz, Greg Hilmas, and Shi Zhang. We arrived in Shanghai on May 7, 2007 at about 2:30 pm local time. We spent three days in Shanghai and then traveled to Changsha on May 10. After the conference, we toured Zhang Jia Jie, which is a national park in the Hunan province, before returning to Shanghai on May 15. We departed Shanghai on May 16.

Interactions with the Shanghai Institute of Ceramics

The Shanghai Institute of Ceramics is part of the Chinese Academy of Sciences. The Academy oversees several institutes, each of which is focused on a specific research area such as metals, ceramics, physics, etc. The Shanghai Institute of Ceramics dates back to 1928 when it was part of the Engineering Institute of Academia Sinica. In 1959, SIC and the Institute for Metals research became independent institutes. The institute has a broad mission that includes fundamental research, applied research and development, engineering research, and production of advanced inorganic materials. One of the primary sources of funding for the institute is a facility that produces and markets single crystals for electronic applications. Currently, the Institute employs approximately 600 research staff. The primary campus consists of four research buildings and student dormitory in Shanghai. The production facility is in an outlying area. The research institute is divided into several laboratories including the State Key Laboratory for High Performance Ceramics and Superfine Microstructures, which is the branch that conducts basic research related to UHTCs. In addition to staff researchers and technicians, the Institute has a graduate education program. Admission to the program is highly competitive. Together with the collective talent of the research staff, the Institute is equipped with a variety of state of the art equipment for materials research, rivaling many of the top Universities in the U.S. A more complete description of the institute and its divisions can be found at http://www.sic.ac.cn/Eindex.htm

Our trip included many technical and social interactions with SIC. Our primary contact at SIC was Dr. Guo-Jun (John) Zhang. Dr. Zhang is a staff researcher in the Nitride Ceramics group at SIC where he conducts research on the synthesis, processing, and characterization of UHTCs and BN-based ceramics. In addition to Dr. Zhang, we spent a great deal of time with Dr. Pei-Ling Wang from SIC. Dr. Wang is the leader of the Group on Nitride Ceramics. As a side note, Dr. Zhang will assume Dr. Wang's position as group leader next year when she retires.

Prior to our arrival in Shanghai, Shi Zhang from UMR worked with Dr. Zhang from SIC to coordinate our trip. The two planned our itinerary for the time in Shanghai, arranged flights to Changsha, planned the tour of Zhang Jia Jie, and coordinated our accommodations for the nights that we were not at the conference hotel. Dr. Zhang acted as our host for our entire trip.

We were met by Dr. Zhang upon our arrival at the Pudong International Airport in Shanghai. The group traveled by bus to the Shanghai hotel. After checking in, Dr. Zhang took us to dinner and then on a walking tour of the Bund area of Shanghai. The next morning, we again met with Dr. Zhang, Dr. Pei-Ling Wang, and a SIC student Wen-Wen Wu. We spent the morning of May 8 touring the Yu Yuan Garden, which is a traditional Chinese garden that dates back over 400 years. At lunch, we were joined by the group from ISTEC, who had arrived in Shanghai during the morning. The group from ISTEC consisted of Dr. Nicola Babini, laboratory director, Dr. Alida Bellosi, staff researcher, and Dr. Frederic Monteverde, also a staff researcher. In the afternoon, the ISTEC group and the UMR group traveled to SIC. The afternoon began with presentations from the visitors to staff and students from SIC. The seminar was attended by Dr. Dongliang Jiang, who is the former director of the State Key Laboratory of High Performance Ceramics and Superfine Microstructures (one of the four main branches of SIC). Dr. Jiang is also an officer of the Chinese Materials Research Society and one of the principal scientists responsible for determining the research direction of the laboratory. The presentations began with Dr. Bellosi, who gave an overview of ISTEC and the UHTC research that is in progress. Next, Drs. Fahrenholtz and Hilmas gave an overview of UMR and the research in the Department of Materials Science and Engineering. The overview included a summary of the UHTC research projects that are in progress at UMR. After the presentations, our group was joined by Dr. Lidong Chen, who is the Deputy Director of SIC. Dr. Chen gave us a tour of the Institute (picture below). Our tour included a visit to the UHTC laboratories where we saw an impressive array of equipment. The group at SIC appears to be particularly well equipped for synthesis and processing of UHTCs with state of the art equipment including a spark plasma sintering furnace, a high temperature hot press, and a 3000°C graphite element furnace. In addition, the group has access to high quality characterization equipment including electron microscopes, x-ray diffraction, and thermal analysis. After our tour, Dr. Chen hosted a banquet for all of the visitors. The next day, Drs. Zhang and Wang led the UMR and ISTEC groups on a tour of Hang Zhou that included visits to West Lake, the Chinese Silk Museum, a tea village, and a Buddist temple. After returning to Shanghai, Drs. Zhang and Wang again hosted a dinner for the group.

During our time with the staff from SIC, we discussed many potential avenues for interactions among UMR, SIC, and ISTEC. Dr. Babini and Dr. Chen met separately to discuss specific paths for interactions between ISTEC and SIC. While no formal discussions were held with Dr. Chen, several conversations were conducted to evaluate potential interactions that included UMR. Based on our initial conversations, UMR, ISTEC, and SIC have agreed to pursue funding for formal interactions that would include exchange of personnel as well as exchanges of specimens that would lead to co-authored presentations and publications. As an initial step, we have tentatively planned to conduct a joint study in which UMR, ISTEC, and SIC will densify a common ZrB_2-based powder using the best available processes at each laboratory. The goal of the study will be to determine how the various processing strategies that are employed by UMR, ISTEC, and SIC affect the microstructure and properties of a common ZrB_2-SiC ceramic.

Tentatively, the plan is for SIC to densify powder by hot pressing, UMR to densify the powder by pressureless sintering using B_4C additions, and ISTEC to densify the powder by pressureless sintering with $MoSi_2$ additions. The resulting ceramics will then be characterized to determine grain size and mechanical properties. For the more formal interactions, each group is going to pursue funding opportunities within their own countries that could support projects that involve exchange of graduate students or other researchers.

Conference Overview

The Fifth China International Conference on High Performance Ceramics (CICC-5) was held on May 10-13 in Changsha, China. The opening ceremony and banquet was held on the evening of May 10. The conference began with four plenary lectures on the morning of May 11 followed by presentations and posters during the afternoon of May 11, May 12, and the morning of May 13. The conference was attended by over 800 people. The program included four plenary talks, around oral 160 presentations, over 600 student posters, and a student speaking competition with about 35 participants.

The UHTC symposium was organized by Dr. Guo-Jun Zhang and a group of international researchers that included representation from ISTEC and UMR. Around 45 abstracts were submitted to the symposium, 15 of which were accepted as oral presentations with the rest assigned to the poster session. This was truly an international symposium with papers from China, Japan, Italy, Turkey, the United Kingdom, Germany, and the United States. The schedule for the oral presentations and the poster titles are attached as an appendix to this document.

The symposium began with an introduction by Dr. Zhang, who briefly summarized the abstracts that were submitted and the organization of the symposium. Then, Greg Hilmas, one of the co-chairs for the first session, presented a brief overview of the need for structural materials for temperatures above 1500°C. The first presentation of the symposium was from Dr. Alida Bellosi, whose invited presentation reviewed the recent work from ISTEC, which focused on densification of ZrB_2, HfB_2, ZrC, and HfC ceramics using $MoSi_2$ as a sintering aid. Her presentation included microstructures, phase analysis, room temperature mechanical properties, and elevated temperature strength for a variety of ceramics. The next presentation was given by Dr. Xing-Hong Zhang from the Harbin Institute of Technology, who was substituting for the scheduled speaker, Dr. Han also from Harbin. The talk focused on the oxidation of ZrB_2-SiC using an arc-heater and a plasma torch. The third presentation in the session was from Dr. Fahrenholtz on reactive processing and oxidation of ZrB_2-SiC. In the final presentation of the first session, Dr. Zhang from SIC discussed his research related to the use of polycarbosilane as a precursor for SiC in ZrB_2-SiC ceramics. The second morning session included two presentations from UMR (Dr. Hilmas and Shi Zhang), a presentation from Dr. Yanchun Zhou of the Institute of Metals Research of the Chinese Academy of Science on Zr-Al-C materials, and a presentation from Dr. Feng Zheng of the South Central University in Changsha on ternary and quaternary phase equilibria. The presentation for Daniel Doni of Imperial College was withdrawn as he was not able to obtain a visa for his trip. The afternoon session included six more UHTC-related presentations including a discussion of the oxidation behavior of sintered UHTCs from Dr. Monteverde from ISTEC. The session was highly successful based on the quality of the contributions as well as attendance. Around 80 people were in the audience for the morning session with nearly the same number for the afternoon.

The poster session was also well attended. The UHTC posters were concentrated in an area of the room that allowed the group to interact. Nearly all of the posters had been prepared by graduate students from Chinese universities, although one unmanned poster was presented by a group from Italy. The session was highly interactive with many questions being asked by the attendees. The student presenters were also very inquisitive and were not shy about asking the attendees their own opinions on topics related to the posters.

The UHTC symposium highlighted several key points related to research in the area. First, the Chinese have a number of groups researching UHTCs at both universities and national laboratories. Both the Shanghai Institute of Ceramics and the Institute for Metals Research have active UHTC research groups. In addition, the Harbin Institute of Technology, the National University of Defense and Technology, the Beijing Institute of Technology, and Tsinghua University have active UHTC research groups. These groups appear to be well funded and well equipped to perform the research. Of particular note, groups from SIC, Tsinghua University, and Beijing Institute of Technology presented work involving spark plasma sintering while the Harbin Institute of Technology has access to arc heater and plasma torch facilities for performance evaluation. The scope of UHTC research and the shear number of active researchers focused on UHTCs appear to far-outweigh the current efforts in the U.S. and Europe.

Other Opportunities for Future Interactions

During the CICC-5 conference, we met several other researchers from Chinese universities and laboratories that were eager to establish collaborations with groups in the U.S. Some of the universities have active UHTC research programs, while others are trying to establish new efforts. Some of the individuals that we met and their research interests are summarized below.

Dr. Yanchun Zhou
Institute for Metals Research, Chinese Academy of Sciences
High Performance Ceramics Division
yczhou@imr.ac.cn

> Dr. Zhou conducts research related to carbide-based materials. He has published his work in English language journals and has attended the International Conference of Advanced Ceramics and Composites held each January in Daytona Beach (formerly Cocoa Beach) Florida.

Dr. Xinghong Zhang
Harbin Institute of Technology
Center for Composite Materials and Structures
zhangxh@hit.edu.cn or zhangxinghong@hotmail.com

> Dr. Zhang has initiated a research program that includes the performance evaluation of ultra-high temperature ceramics. His presentation in Changsha summarized a great deal of research that included arc-heater testing and oxidation in a high temperature torch rig. Dr. Zhang and his colleagues from Harbin issued an open invitation for us to visit their institution.

Dr. Feng (Frank) Zheng
Central South University
Changsha, Hunan, China

Dr. Zheng conducts research related to phase equilibria in ceramics. His program focuses on thermodynamic calculations and computer-aided development of phase diagrams. Dr. Zheng spent around 10 years in the U.S. at the Pacific Northwest National Laboratory and completing his PhD at the University of Washington. His current institution is a large regional university, but the emphasis is more toward teaching than research. Dr. Zheng would welcome opportunities that would allow him to work in the U.S. during summers.

Dr. Jiahu Ouyang
Institute for Advanced Ceramics
Harbin Institute of Technology
ouyangih@hit.edu.cn

General interest in UHTCs

Dr. Yujin Wang
Institute for Advanced Ceramics
Harbin Institute of Technology
wangyuj@hit.edu.cn

General interest in UHTCs

Dr. Yiquang Wang
Northwestern Polytechnical University
National State Key Laboratory of Thermostructure Composite Materials
Yiquang.wang@gmail.com

General interest in UHTCs

Dr. Changchun Ge
University of Science and Technology Beijing
School of Materials Science and Engineering
Director of the Institute of Special Ceramics and Powder Metallurgy
ccge@mater.ustb.edu.cn or ustbgcc@163.com

General interest in UHTCs

Part of our tour of the Shanghai Institute of Ceramics. Front row: Guo-Jun Zhang, Alida Bellosi, Lidong Chen, Pei-Ling Wang. Back row: Frederick Monteverde, Greg Hilmas, Nicola Babini, Bill Fahrenholtz, Shi Zhang.

Appendix. UHTC talks and posters from CICC-5.

Student Speaking Contest (UHTC talks highlighted)

Afternoon, May 11 — Yuhua Hall (B)

Oral Presentation Competition for Domestic Students (Preliminary)

Chair: Chang-An WANG (*Tsinghua University, China*)

13:50	E094	**Mechanical-activation-assisted combustion synthesis of SiC powders at low nitrogen pressures** K. Yang (*Technical Institute of Physics and Chemistry, China*)
14:05	E098	**Preparation of ultrafine β-SiC particles and nanorods by reducing silica sol with amylum** F. Wang (*University of Science and Technology Beijing, China*)
14:20	E189	**Microstructural evolution of Ti_3AlC_2 during the processing of Cu-Ti_3AlC_2 composites** J. Zhang (*Institute of Metal Research, China*)
14:35	E194	**Mechanical properties of bulk $Zr_2Al_4C_5$ ceramic** L.F. He (*Institute of Metal Research, China*)
14:50	G014	**Preparation and evaluation of the heavy-duty and anti-wear nano-ceramic epoxy coating** W.W. Cong (*University of Science and Technology Beijing, China*)
15:05	G028	**Preparation of compound ceramic coatings on Ti-6Al-4V alloy by surface nanocrystallization/micro-plasma oxidation** G.D. Hao (*Harbin Institute of Technology, China*)
15:20	Break	
15:25	F051	**Investigation of the bioactivity of $CaSiO_3/Ti_3SiC_2$ composites** S.J. Zhao (*Shanghai Institute of Ceramics, China*)
15:40	F063	**Preparation of hydroxyapatite coatings on carbon/carbon composites by a hydrothermal electrodeposition process** G.Y. Zhu (*Shaanxi University of Science and Technology, China*)
15:55	F066	**In vitro degradation studies on preparation of calcium phosphate glass-ceramics as drug delivery biomaterials** Z. Zhang (*Tianjin University, China*)
16:10	F070	**The influence of multiple firing on wear behavior of dental veneering ceramic** Q.P. Gao (*Central South University, China*)
16:25	E240	**Study on the microstructures of three kinds of solid FeS** L.N. Zhu (*Academy of Armored Forces Engineering, China*)
16:40	Break	
16:45	SA021	**In-situ synthesis of ultra-fine ZrB_2-SiC composite powders via sol-gel method** Y.J. Yan (*Shanghai Institute of Ceramics, China*)
17:00	SA024	**Reactive synthesis of ZrB_2-SiC-ZrC ultra high temperature ceramics** W.W. Wu (*Shanghai Institute of Ceramics, China*)
17:15	SA035	**Combustion synthesis of Si_3N_4 with Si/NH_4Cl under nitrogen pressure of 2 MPa** Y.X. Chen (*Technical Institute of Physics and Chemistry, China*)
17:30	SA037	**Effects of oxygen content on the properties of super-high-temperature resistant Si-Al-C fibers** D.F. Zhao (*National University of Defense Technology, China*)
17:45	SB014	**Preparation of nano-laminated composite by electrophoretic deposition** W. Lin (*Tsinghua University, China*)
18:00	SB017	**Investigation of Ti/Al_2O_3 and Ni/Al_2O_3 laminates prepared by plasma activated sintering (PAS)** J.P. Lin (*Xi'an Jiaotong University, China*)

UHTC Presentations

Morning, May 12 ♦ Hunan Hall (A)

Oral Presentations

International Symposium on Ultra-High Temperature Ceramics

Co-Chair: Gian N. BABINI (*ISTEC-CNR, Italy*)
Co-Chair: Greg E. HILMAS (*University of Missouri-Rolla, USA*)

07:55 Welcome Address

08:10 SA001 Invited — **Development and characteristics of particulate composites based on ultra-refractory borides and carbides**
A. Bellosi (*ISTEC-CNR, Italy*)

08:35 SA002 Invited — **Characteristics and mechanisms of dynamic oxidation for ZrB_2-SiC based UHTC**
J.C. Han (*Harbin Institute of Technology, China*)

09:00 SA003 Invited — **Reactive processing and oxidation of ZrB_2-SiC ceramics**
W.G. Fahrenholtz (*University of Missouri-Rolla, USA*)

09:25 SA005 Invited — **Preparation and microstructure tailoring of ZrB_2-based ultra-high temperature ceramics (UHTCs)**
G.J. Zhang (*Shanghai Institute of Ceramics, China*)

International Symposium on Ultra-High Temperature Ceramics

Co-Chair: William G. FAGRENHOLTZ (*University of Missouri-Rolla, USA*)
Co-Chair: Guo-Jun ZHANG (*Shanghai Institute of Ceramics, China*)

10:00 SA004 Invited — **Structure-property relations in monolithic and fibrous monolithic ZrB_2-based ceramics**
G.E. Hilmas (*University of Missouri-Rolla, USA*)

10:25 SA028 Invited — **Zirconium carbide/tungsten (ZrC/W) composite prepared by *in-situ* reaction sintering processing**
S.C. Zhang (*University of Missouri-Rolla, USA*)

10:50 SA030 Invited — **New ternary carbides in Zr-Al-C system for ultrahigh temperature applications**
Y.C. Zhou (*Institute of Metal Research, China*)

11:15 SA032 Invited — **TEM of UHTCs: microstructure development and densification mechanisms**
D.J. Daniel (*Imperial College London, UK*)

11:40 SA031 Invited — **Phase relationships in ultra-high temperature materials**
F. Zheng (*Central South University, China*)

Afternoon, May 12 ♦ Hunan Hall (A)

Oral Presentations

International Symposium on Ultra-High Temperature Ceramics

Co-Chair: Alida BELLOSI (*ISTEC-CNR, Italy*)
Co-Chair: Feng ZHENG (*Central South University, China*)

14:00	SA038 Invited	**Processing and characterization of ultra-high temperature oxide fibre-reinforced oxide ceramic matrix composites with improved thermomechanical properties** C. Kaya (*Yildiz Technical University, Turkey*)
14:25	SA023	**Ultra-refractory ZrB_2-based ceramics under simulated atmospheric re-entry conditions** F. Monteverde (*National Research Council, Italy*)
14:45	SA029	**Effect of iron additive on the sintering behavior of hot-pressed ZrC-W composites** Y.J. Wang (*Harbin Institute of Technology, China*)
15:05	SA034	**Oxyacetylene ablation behavior of carbon fibers reinforced carbon matrix and ultra-high temperature ceramics composites** S.F. Tang (*Institute of Metal Research, China*)
15:25	SA036	**Fabrication and properties of 2D C/SiC-TaC UHTCC** Y.D. Zhang (*National University of Defense and Technology, China*)
15:45	SA041	**Microstructure and mechanical properties of high density PCBN aggregates** X.J. Ren (*Liverpool John Moores University, UK*)

Session E: Engineering Ceramics and Composites

Chair: Long-Hao QI (*Tsinghua University, China*)

16:15	E143 Invited	**The effect of powder nanostructurization by the high-energy milling on densification of β-SIALON ceramics** M. Sopicka-Lizer (*Silesian University of Technology, Poland*)
16:40	E141	**SiAlON ceramics from low cost β-Si_3N_4 powder** F. Kara (*Anadolu University, Turkey*)
17:00	E142	**Optimization of α-SiAlON microstructure by heat treatment** S. Kurama (*Anadolu University, Turkey*)
17:20	E150	**Spark plasma sintering of α-β SiAlON-TiN composites** A. Kara (*Anadolu University, Turkey*)
17:40	E142A	**Influence of compositional design on the cutting behavior of SiAlON ceramics** H. Mandal (*Anadolu University, Turkey*)

Partial Listing of Posters (UHTC Posters Highlighted)

[172] (H010) The use of Angang slag for the production of glass-ceramic materials H.X. Lu (*Zhengzhou University, China*)

[173] (H012) Effect of ZrO_2 on mechanical and biological properties of calcium phosphate-based glass-ceramics for biomedical applications C.Y. Zheng (*Institute of Metal Research, China*)

[174] (H014) Property optimization design on glass with B_2O_3 base composition for PDP rib Y.S. Kim (*Pusan National University, Korea*)

[175] (H016) Laser induced crystallization mechanism of Li_2O–Al_2O_3–SiO_2 (LAS) glass system and its characterization K.H. Lee (*Pusan National University, Korea*)

[176] (H017) BaO-B_2O_3-SiO_2 glass powders prepared by ultrasonic spray pyrolysis S.K. Hong (*Konkuk University, Korea*)

[177] (H023) Comparison of the DC and AC conductivities of Li_2O-P_2O_5 glass J.Y. Pan (*Changchun Institute of Applied Chemistry, China*)

[178] (H024) Impedance study of $33.3Na_2O$-$(66.7-x)B_2O_3$-xP_2O_5 glasses Y.J. Jung (*Pusan National University, Korea*)

[179] (H027) Preparation and characterization of the sol-gel derived bioactive glass-fibers X.F. Chen (*South China University of Technology, China*)

[180] (H028) The possibility of glass storage device with long term preservation and high density adopted Nd:YAG laser Y.H. Kim (*Pusan National University, Korea*)

[181] (SA007) Effect of glass phase on the thermal shock resistance of ZrB_2-SiC ultra high temperature ceramic S.Z. Zhu (*Beijing Institute of Technology, China*)

[182] (SA008) Microstructure and mechanical properties of SiC whisker-reinforced ZrB_2 ultra-high temperature ceramic P. Hu (*Harbin Institute of Technology, China*)

[183] (SA009) Effects of holding time on properties of ZrB_2-SiC composite using the spark plasma sintering reactive synthesis method Y. Zhao (*Shanghai Institute of Ceramics, China*)

[184] (SA010) Efficient synthesis/sintering routes to obtain fully dense ZrB_2-SiC UHTC materials G. Cao (*Università degli Studi di Cagliari, Italy*)

[185] (SA011) Microstructure and mechanical properties of ZrB_2- based UHTC via reactive hot pressing Q. Qu (*Harbin Institute of Technology, China*)

[186] (SA012) Preparation and property of ZrB_2-based laminated composites sintered by spark plasma sintering H.L. Wang (*Tsinghua University, China*)

[187] (SA013) Effect of the rare earth oxides on sintering behavior and microstructure of ZrB_2–SiC ceramics X.Y. Li (*Harbin Institute of Technology, China*)

[188] (SA015) Microstructure of ZrB_2–SiC composite by spark plasma sintering J.L. Cao (*Beijing Institute of Technology, China*)

[189] (SA016) Ablation resistant of pressureless sintered ZrB_2-based ceramics Z.Q. Cheng (*Shandong Research & Design Institute of Industrial Ceramics, China*)

[190] (SA017) Pressureless sintering of ultra-high temperature ZrB_2-SiC ceramics C.L. Zhou (*Shandong Research & Design Institute of Industrial Ceramics, China*)

[191] (SA018) Study on oxidation kinetics of ZrB_2-SiC composites T.Y. Tian (*Shandong Research & Design Institute of Industrial Ceramics, China*)

[192] (SA019) Oxidation of short carbon fiber reinforced ZrB_2-SiC ceramics under atmospheric and oxyacetylene torch conditions F.Y. Yang (*Harbin Institute of Technology, China*)

[193] (SA020) Preparation and characterization of stable ZrB_2-based ultra-high temperature ceramics slurry by aqueous gelcasting H. Zhang (*Shanghai Institute of Ceramics, China*)

[194] (SA026) Properties and microstructure of an HfB_2-HfC-SiC ultra-high temperature ceramics J.P. Li (*Harbin Institute of Technology, China*)

[195] (SA027) Thermodynamic assessment of the Zr-Si-C system H.M. Chen (*Central South University, China*)

[196] (SA039) Study on thermal shock resistance of ultra-high temperature ceramics W.G. Li (*Tsinghua University, China*)

[197] (SA040) Investigation on fracture strength of ultra-high temperature ceramics T. Zeng (*Harbin University of Science and Technology, China*)

[198] (SA042) Mechanical properties evaluation of ultra-high temperature ceramics X.X. Bu (*China Building Materials Academy, China*)

[199] (SB009) Microstructure and dielectric properties of $Li_xTi_yNi_{1-x-y}O$ thin films C.H. Zhao (*University of Science and Technology Beijing, China*)

[200] (SB011) A stepwise route to the preparation of layered double hydroxides (LDHs) Z.H. Liu (*Donghua University, China*)

[201] (SB015) Preparation of glass-alumina functionally gradient materials by rapidly prototyping technology H.T. Jiang (*Shaanxi University of Science & Technology, China*)

[202] (SB016) Microstructure and mechanical properties of freeze cast alumina/zirconia layered composites J.M. Lee (*Pusan University, Korea*)

[203] (SB018) Research of TiN/Al_2O_3 functionally gradient material fabricated by in-situ reaction J.H. Nie (*Wuhan University of Science and Technology, China*)

[204] (SB019) Corrosion protection of stainless steel by ZrO_2-CeO_2 sol-gel coatings J.X. Ye (*Chongqing University, China*)

[205] (SB020) Fabrication of SiC dense-porous laminates by electrophoretic deposition techniques Y. Li (*Xi'an Jiaotong University, China*)

[206] (SB022) Dynamic observation of fracture process in a silicon carbide-matrix laminated ceramic composite Y. Zhou (*Beijing Jiaotong University, China*)

[207] (SB023) Microstructure and properties of bulk Ta_2AlC and Ta_4AlC_3 ceramics prepared by an in-situ synthesis/hot pressing method C.F. Hu (*Institute of Metal Research, China*)

[208] (SB024) Research on the preparation of ternary layered Ti_3SiC_2 ceramic by SHS/PHIP Y.L. Bai (*Harbin Institute of Technology, China*)

[209] (SB026) Fabrication and mechanical properties of B_4C/BN laminated ceramics W.L. Liu (*University of Science & Technology Beijing, China*)

[210] (SB028) Joining $CoSb_3$ to metal surface of FGM electrode for thermoelectric modules by SPS T. Sui (*Tsinghua University, China*)

[211] (SB029) Study on splat formation of plasma sprayed functionally graded YSZ/NiCrCoAlY thermal barrier coatings Z. Ma (*Beijing Institute of Technology, China*)

[212] (SB032) Preparation and properties of multilayered mullite/Mo functional gradient materials S.H. Chen (*Guilin University of Technology, China*)

[213] (SB033) Preparation of Mg-W density graded materials by spark plasma sintering technique Q. Shen (*Wuhan University of Technology, China*)

[214] (SB034A) Cladding of WC-Cr_3C_2 cermets coating by laser controlled reactive synthesize W.G. Li (*Shanghai University of Engineering Science, China*)

[215] (SB035) High-speed sliding mild wear behaviour of WC_p-reinforced iron matrix gradient composites Y.P. Song (*Henan University of Science and Technology, China*)

[216] (SB035A) Synthesis and characterization of TiB_2-Ni-Ni_3Al-405 steel graded material by field-activated SHS S.P. Chen (*Taiyuan University of Technology, China*)

[217] (SB036) A technology to fabricate site-selectively nanomaterials on flexible substrate L. Xing (*Graduate University of Chinese Academy of Science, China*)

[218] (SC010) Characterization of phase transitions in lead-free piezoelectric ceramics $(K_{0.5}Na_{0.5})_{1-x}Li_xNbO_3$ near MPB composition K. Wang (*Tsinghua University, China*)

[219] (SC011) Effect of addition of MnO_2 on piezoelectric properties of $(K_{0.5}Na_{0.5})NbO_3$-$LiNbO_3$ lead-free piezoelectric ceramics H.L. Du (*Northwestern Polytechnical University, China*)

APPENDIX B: M.S. THESIS OF MICHAEL TEAGUE

Michael P. Teague completed his M.S. thesis during the course of this project. The thesis was titled "Modeling and Measurement of Thermal Residual Stresses and Isotope Effects on Thermo Physical Properties of ZrB_2-SiC Ceramics" and is available through the library at Missouri S&T. The two main chapters of the thesis are manuscripts. The first has been published while the second is in preparation at this time. The citations are:

1. M.P. Teague. G.E. Hilmas, and W.G. Fahrenholtz, "Finite Element Modeling of Internal Stress Factors for ZrB_2-SiC Ceramics," accepted for publication in the 32nd Annual International Conference on Advanced Ceramics and Composites, January 27-February 1, 2008, Daytona Beach, FL.
2. M.P Teague, G.E. Hilmas, and W.G. Fahrenholtz, "Processing and Thermal Properties of ZrB_2-SiC Ceramics made with Isotopically Pure ^{11}Boron," to be submitted to the Journal of the American Ceramic Society.

Abstract

Commercially available finite element modeling software (ABAQUS) was used to investigate the internal residual stresses that develop as a result of cooling from processing temperatures in ZrB_2-SiC ceramics. The size and shape of the SiC particles were varied to evaluate their effect on the residual stresses. Results were compared to experimental data and showed similar trends, where increasing SiC particle size increased tensile stress and also decreased strength. Alternative SiC particle shapes were created and modeled in an attempt to reduce residual stress. Models were used to analyze potential benefits of novel spiral shaped SiC inclusions and were also used to better understand the short comings of the composites.

An attempt to validate the models using neutron diffraction to measure residual stress led to the fabrication of ZrB_2-SiC composites made using isotopically pure ^{11}B and a reaction hot pressing technique. Natural boron in the conventional ZrB_2 ceramics had to be replaced with the ^{11}B (0.0055 barns) due to the high thermal neutron absorption of natural boron (767 barns). Neutron diffraction experiments were successfully performed at Argonne National Laboratory, however, stress free reference samples for ZrB_2 and SiC must still be measured to complete the residual stress analysis.

ZrB_2-SiC ceramics made from ^{11}B were characterized to confirm a complete reaction and full density. The microstructure was compared to natural B ZrB_2-SiC ceramics to confirm equivalent grain size. Effects on the thermal properties by the ^{11}B isotope were studied by measuring thermal diffusivity of both natural boron and ^{11}B containing ZrB_2-SiC specimens at Oak Ridge National Laboratory. The thermal conductivity and thermal expansion were both determined to be lower for the ^{11}B containing materials.

APPENDIX C: PHD DISSERTATION OF JAMES ZIMMERMANN

James Zimmermann completed his Ph.D. Dissertation during the course of this project. Jim started his research under the previous AFOSR project (F49620-03-1-0072) at Missouri S&T (then University of Missouri-Rolla). The thesis was titled "Improving the Thermal Shock Resistance of Zirconium Diboride Ceramics" and is available through the Missouri S&T library. The four main chapters of the thesis were published as journal papers. The citations are:

1. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Thermal Shock Resistance and Fracture Behavior of ZrB_2-Based Fibrous Monolith Ceramics," Journal of the American Ceramic Society, 92(1) 161-166 (2009).
2. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Thermal Shock Resistance of ZrB_2 and ZrB_2-30% SiC, Materials Chemistry and Physics, 112(1) 140-145 (2008).
3. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, R. Dinwiddie, W. Porter, and H. Wang, "Thermophysical Properties of ZrB_2-Based Ceramics," Journal of the American Ceramic Society, 91(5) 1405-1411 (2008).
4. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, F. Monteverde, and A. Bellosi, "Fabrication and Properties of Reactively Hot Pressed ZrB_2-SiC Ceramics," Journal of the European Ceramic Society, 27(7) 2729-2736 (2007).

Abstract

Zirconium diboride (ZrB_2) and ZrB_2 – SiC ceramics with densities greater than 99% were fabricated by hot pressing ZrB_2 and SiC powders and reactively hot pressing ZrH_2, B_4C and Si to form ZrB_2-27 vol% SiC. Thermophysical properties were investigated for hot pressed ZrB_2 and ZrB_2-30 vol% SiC ceramics. The thermal conductivity of ZrB_2 increased from 56 W m^{-1} K^{-1} at room temperature to 67.0 W m^{-1} K^{-1} at 1675 K, whereas the thermal conductivity of ZrB_2-SiC decreased from 62.0 W m^{-1} K^{-1} to 56 W m^{-1} K^{-1} over the same temperature range. Electron and phonon contributions to thermal conductivity were determined using electrical resistivity measurements and were used, along with grain size models, to explain the observed trends. Thermal shock of high density ZrB_2, ZrB_2 - 30 vol% SiC and ZrB_2- 30 vol% SiC / graphite – 15 vol% SiC fibrous monoliths was studied. Experimental thermal shock values measured during a water quench test were the same for both materials (ΔT_{crit} = ~400°C). A finite element model was used to estimate the temperature gradients and stresses in both ceramics during quench testing. The model predicted that maximum thermal stresses exceeded the strength of ZrB_2 (568 MPa) but not ZrB_2-30 vol% SiC (863 MPa). The lower than predicted thermal shock resistance of ZrB_2-SiC was attributed to the non-uniform cooling between the ZrB_2 matrix and the SiC particulate phase. Water quench thermal shock testing of ZrB_2-based fibrous monolith ceramics had a critical thermal shock temperature (ΔT_{crit}) of 1400°C, a 250% improvement over the previously reported ΔT_{crit} values of ZrB_2 and ZrB_2-30vol.% SiC of similar dimensions (4 x 3 x 45 mm). The improvement in thermal shock resistance was attributed to cell boundary crack propagation and crack deflection around the load bearing cells.

APPENDIX D: INFORMATION ON OTHER RESEARCH PROJECTS

The research effort on ultra-high temperature ceramics at Missouri S&T (then University of Missouri-Rolla) began in January 2003 with funding from AFOSR (F49620-03-1-0072). Over the next several years, UHTC research was supported by grants a variety of federal agencies and companies. The support allowed the group to assemble the processing, characterization, and testing facilities needed to investigate materials for extreme environments, which often require extreme processing and testing conditions. The diversity of projects also gave the group the resources to build informal and formal collaborations with other UHTC researchers from around the world. The synergistic nature of the projects allowed the Missouri S&T group to become the premier organization in the U.S. for fundamental research on the processing, microstructure, properties, and performance of UHTCs. The lists below reflect the current and previous research projects, research facilities established, publications, thesis/dissertations, and patent applications filed based on the UHTC research activity at Missouri S&T as of January 2009.

UHTC Research Projects at Missouri S&T

The list below summarizes the UHTC-related research projects that have been funded at Missouri S&T. Since 2003, the UHTC research group has grown to as many as nine graduate students and two research scientists.

1. Defense University Research Instrumentation Program
   Acquisition of an Ultra-High Temperature Laser Flash Thermal Properties Analyzer
   $260,625, 4/1/08-3/31/09
2. Air Force Research Laboratory
   Project 9.3.2 High Temperature Thermomechanical Behavior of UHTCs
   $120,000, 8/1/07-7/30/08
   Co-Principal Investigator, 50% Shared Credit (G. Hilmas PI)
3. Air Force Research Laboratory
   Project 9.3.1 Improved Oxidation Stability and Arc Heater Testing of UHTC's
   $96,000, 10/1/06-4/29/08
4. Air Force Office of Scientific Research
   Design of Ultra-High Temperature Ceramics for Improved Performance
   $450,000, 3/06-12/08
   Principal Investigator, 50% Shared Credit (G. Hilmas Co-PI)
5. Advanced Ceramics Research
   Phase II - High Strength Carbide Based Fibrous Monolith Materials for Solid Rocket Nozzles
   $300,000, 10/05-9/07
6. Naval Surface Warfare Center
   Graduate Student Research Support
   $7200, 6/05-11/05

7. Air Force Research Laboratory
   Fabrication and Testing of UHTC Components for Thermal Protection and Propulsion Applications
   $120,000, 5/05-4/07

8. Defense University Research Instrumentation Program
   Acquisition of a High Temperature Mechanical Testing System
   $135,000, 4/05-3/06

9. Advanced Ceramics Research (MDA STTR program)
   TaC-Based Fibrous Monolithic Ceramics
   $30,000, 8/04-2/05

10. National Science Foundation
    CAREER: Reactive Processing of High Temperature Materials
    $400, 000, 6/04-5/09

11. Air Force Research Laboratory
    Development of Scale-Up Processes to Enable the Production of Ceramic Composites for Service Temperatures in Excess of 2000°C
    $113,500, 6/04-5/06

12. National Science Foundation
    NSF-AFOSR Joint Workshop on Future Ultra-High Temperature Materials
    $31,340, 1/04-12/04

13. Air Force Office of Scientific Research
    Reactive Processing and Co-Extrusion of Ultra-High Temperature Ceramics
    $300,000, 1/03-12/05
    Principal Investigator, 50% shared credit (G. Hilmas co-PI)

14. U.S. Army Space and Missile Defense Command
    Processing-Property-Microstructure Relationships in SiC-based Ceramics
    $400,000, 8/03-7/06

Research Facilities Established as Part of the UHTC projects

Several laboratory facilities were established to support the processing, characterization and testing efforts at Missouri S&T. The list below summarizes the facilities that were directly linked to UHTC projects. The UHTC group also made use of other facilities available at the university, which are not listed.

1. Ultra-high temperature thermal properties analyzer
   - Purchased as part of a DURIP grant
   - Thermal diffusivity and heat capacity from cryogenic temperatures to 2800°C
2. Ultra-high temperature mechanical testing facility
   - Designed and built as part of a DURIP grant
   - Modified an existing test frame for mechanical testing up to ~2500°C in controlled atmosphere
   - Purchased a new load frame for mechanical testing in air up to 1500°C
3. Hot Pressing Capabilities

- Thermal technology HP20-3060 hot press with a 3 inch diameter hot zone for temperatures up to ~2400°C
- Thermal technology HP50-7010-graphite hot press with a hot zone 7 inches in diameter for temperatures up to 2300°C.

Publications

1. A.A. Buchheit, G.E. Hilmas, W.G. Fahrenholtz, and D.M. Deason, "Thermal Shock Resistance of an AlN-BN-SiC Ceramic," submitted to the Journal of the American Ceramic Society, December 11, 2008.
2. S.C. Zhang, W.G. Fahrenholtz, and G.E. Hilmas, "Oxidation of ZrB_2 and ZrB_2-SiC Ceramics with Tungsten Additions," submitted to Transactions of the Electrochemical Society, Proceedings of the 214[th] Meeting of the Electrochemical Society, November 18, 2008.
3. G.E. Hilmas and W.G. Fahrenholtz, "Ultra-High Temperature Ceramics for Applications in Extreme Environments," to be published in "Global Roadmap for Ceramics – Proceedings of the Second International Ceramics Congress," ed. by N. Babini and A. Bellosi, June 29-July 4, 2008, Verona, Italy.
4. J. Marschall, D.A. Pejakovi, W.G. Fahrenholtz, G.E. Hilmas, S. Zhu, J. Ridge, D.G. Fletcher, C.O. Asma, O. Chazot, and J. Thömel, "Oxidation of ZrB_2-SiC Ultra-High Temperature Ceramic Composites in Dissociated Air," submitted to the Journal of Thermophysics and Heat Transfer, July 20, 2008.
5. M.P. Teague. G.E. Hilmas, and W.G. Fahrenholtz, "Finite Element Modeling of Internal Stress Factors for ZrB_2-SiC Ceramics," accepted for publication in the 32[nd] Annual International Conference on Advanced Ceramics and Composites, January 27-February 1, 2008, Daytona Beach, FL.
6. M. Playez, D.G. Fletcher, J. Marschall, W.G. Fahrenholtz, G.E. Hilmas, and S. Zhu, "Optical Emission Spectroscopy During Plasmatron Testing of ZrB_2-SiC Ultra-High Temperature Ceramic Composites," submitted to the Journal of Thermophysics and Heat Transfer, July 20, 2008.
7. A.A. Buchheit, G.E. Hilmas, W.G. Fahrenholtz, and D.M. Deason, "Thermal Shock Resistance of an AlN-BN-SiC Ceramic," submitted to Materials Science and Engineering A, October 30, 2007.
8. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Thermal Shock Resistance and Fracture Behavior of ZrB_2-Based Fibrous Monolith Ceramics," Journal of the American Ceramic Society, 92(1) 161-166 (2009).
9. X. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Densification and Mechanical Properties of TaC-Based Ceramics," Materials Science and Engineering A, 501(1-2) 37-43 (2009).
10. X. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Densification, Mechanical Properties, and Oxidation of TaC-TaB_2," Journal of the American Ceramic Society, 91(12) 4129-4132 (2008).
11. S.C. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Improved Oxidation Resistance of Zirconium Diboride by Tungsten Carbide Additions," Journal of the American Ceramic Society, 91(11) 3530-3535 (2008).

12. S.E. Landwehr, G.E. Hilmas, W.G. Fahrenholtz, I.G. Talmy, and S.G. DiPietro, "Microstructure and Mechanical Characterization of ZrC-Mo Cermets Produced by Hot Isostatic Pressing," Materials Science and Engineering A, 497(1-2) 79-86 (2008).
13. J.W. Zimmermann, G.E. Hilmas, and W.G. Fahrenholtz, "Thermal Shock Resistance of ZrB_2 and ZrB_2-30% SiC, Materials Chemistry and Physics, 112(1) 140-145 (2008).
14. A.A. Buchheit, G.E. Hilmas, W.G. Fahrenholtz, D.M. Deason, and H. Wang, "Thermal Properties of a Reaction Hot Pressed $Mo_{\leq 5}Si_3C_{\leq 1}$ Ceramic," Intermetallics, 16(9) 1047-1052 (2008).
15. A.A. Buchheit, G.E. Hilmas, W.G. Fahrenholtz, D.M. Deason, and H. Wang, "Mechanical and Thermal Properties of an AlN-BN-SiC Ceramic," Materials Science and Engineering A, 494(1-2) 239-246 (2008).
16. X. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Synthesis, Densification, and Mechanical Properties of TaB_2," Materials Letters, 62(27) 4251-4253 (2008).
17. A.A. Buchheit, G.E. Hilmas, W.G. Fahrenholtz, D.M. Deason, and H. Wang, "Processing and Thermal Properties of an Mo_5Si_3C-SiC Ceramic," Intermetallics, 16(7) 854-859 (2008).
18. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, R. Dinwiddie, W. Porter, and H. Wang, "Thermophysical Properties of ZrB_2-Based Ceramics," Journal of the American Ceramic Society, 91(5) 1405-1411 (2008).
19. W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, and S. Zhu, "Pressureless Sintering of Zirconium Diboride: Particle Size and Additive Effects," Journal of the American Ceramic Society, 91(5) 1398-1404 (2008).
20. S. Zhu, W.G. Fahrenholtz, and G.E. Hilmas, "Enhanced Densification and Mechanical Properties of ZrB_2-SiC Processed by a Preceramic Polymer Coating Route," Scripta Materialia, 59(1) 123-126 (2008).
21. S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, S.C. Zhang, E.J. Yadlowsky, and M.D. Keitz "Microwave Sintering of Zirconium Diboride," Composites A, 39(3) 449-453 (2008).
22. S.E. Landwehr, G.E. Hilmas, W.G. Fahrenholtz, and I.G. Talmy, "Processing of ZrC-Mo Cermets for High Temperature Applications, Part II: Pressureless Sintering and Mechanical Properties," Journal of the American Ceramic Society, 91(3) 873-878 (2008).
23. S.C. Zhang, G. Hilmas, and W.G. Fahrenholtz, "Pressureless Sintering of ZrB_2-SiC Ceramics," Journal of the American Ceramic Society, 91(1) 26-32 (2008).
24. S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, and S.C. Zhang, "Pressureless Sintering of Zirconium Diboride Using Boron Carbide and Carbon Additions," Journal of the American Ceramic Society, 90(11) 3660-63 (2007).
25. H.J. Brown-Shaklee, W.G. Fahrenholtz, and G.E. Hilmas, "Densification of Hot-Pressed HfB_2 Ceramics with Carbon and B_4C Additions," pp. 1056-1060 in Proceedings of the 10th International Conference, June 17-21, 2007, Berlin, Germany, ed. by J.G. Heinrich and C. Aneziris, Goller Verlag, Baden-Baden (2007).
26. M.C. Malone, S.C. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Thermodynamic Approach to Reaction Processing of W-Ta-C Composite Materials," pp. 1168-1172 in Proceedings of the 10th International Conference, June 17-21, 2007, Berlin, Germany, ed. by J.G. Heinrich and C. Aneziris, Goller Verlag, Baden-Baden (2007).
27. T. Huang, G.E. Hilmas, W.G. Fahrenholtz, and M.C. Leu, "Dispersion of Zirconium Diboride in an Aqueous, High Solids Paste," International Journal of Applied Ceramic Technology, 4(5) 470-479 (2007).

28. S. Henderson, W.G. Fahrenholtz, G.E. Hilmas, and J. Marschall, "High-Velocity Impact Resistance of ZrB_2-SiC," Ceramic Engineering and Science Proceedings, 27(2) 3-10 (2007).
29. S.E. Landwehr, G.E. Hilmas, W.G. Fahrenholtz, and I.G. Talmy, "Processing of ZrC-Mo Cermets for High Temperature Applications, Part I: Chemical Interactions in the ZrC-Mo System," Journal of the American Ceramic Society, 90(7) 1998-2002 (2007).
30. S.C. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Zirconium Carbide-Tungsten Cermets Prepared by In-Situ Reaction Sintering," Journal of the American Ceramic Society, 90(6) 1930-1933 (2007).
31. W.G. Fahrenholtz, G.E. Hilmas, I.G. Talmy, and J.A. Zaykoski, "Refractory Diborides of Zirconium and Hafnium," Journal of the American Ceramic Society, 90(5) 1347-1364 (2007).
32. S. Zhu, W.G. Fahrenholtz, G.E. Hilmas, and S.C. Zhang, "Pressureless Sintering of Carbon-Coated Zirconium Diboride Powders," Materials Science and Engineering A, 459 167-171 (2007).
33. A. Rezaie, W.G. Fahrenholtz, and G.E. Hilmas, "Effect of Hot Pressing Time and Temperature on the Microstructure and Mechanical Properties of ZrB_2-SiC," Journal of Materials Science, 42(8) 2735-2744 (2007).
34. J.W. Zimmermann, G.E. Hilmas, W.G. Fahrenholtz, F. Monteverde, and A. Bellosi, "Fabrication and Properties of Reactively Hot Pressed ZrB_2-SiC Ceramics," Journal of the European Ceramic Society, 27(7) 2729-2736 (2007).
35. X. Zhang, G.E. Hilmas, W.G. Fahrenholtz, and D.M. Deason "Hot Pressing of Tantalum Carbide with and without Sintering Aids," Journal of the American Ceramic Society, 90(2) 393-401 (2007).
36. A. Rezaie, W.G. Fahrenholtz, and G.E. Hilmas, "Evolution of Structure During the Oxidation of Zirconium Diboride-Silicon Carbide in Air up to 1500°C," Journal of the European Ceramic Society, 27(6) 2495-2501 (2007).
37. W.G. Fahrenholtz, "Thermodynamic Analysis of ZrB_2-SiC Oxidation: Formation of a SiC-Depleted Region," Journal of the American Ceramic Society, 90(1) 143-148 (2007).
38. S. Zhu, W.G. Fahrenholtz, and G.E. Hilmas, "Influence of Silicon Carbide Particle Size on the Microstructure and Mechanical Properties of Zirconium Diboride-Silicon Carbide Ceramics," Journal of the European Ceramic Society, 27(4) 2077-2083 (2007).
39. A.L. Chamberlain, W.G. Fahrenholtz and G.E. Hilmas, "Low Temperature Densification of Zirconium Diboride Ceramics by Reactive Hot Pressing," Journal of the American Ceramic Society, 89(12) 3638-3645 (2006).
40. A. Rezaie, W.G. Fahrenholtz, and G.E. Hilmas, "Oxidation of Zirconium Diboride-Silicon Carbide at 1500°C in a Low Partial Pressure of Oxygen," Journal of the American Ceramic Society, 89(10) 3240-3245 (2006).
41. S.C. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Pressureless Densification of Zirconium Diboride with Boron Carbide Additions," Journal of the American Ceramic Society, 89(5) 1544-1550 (2006).
42. W.G. Fahrenholtz, "Reactive Processing in Ceramic-Based Systems," International Journal of Applied Ceramic Technology, 3(1) 1-12 (2006).
43. A.L. Chamberlain, W.G. Fahrenholtz, and G.E. Hilmas, "Pressureless Sintering of Zirconium Diboride," Journal of the American Ceramic Society, 89(2) 450-456 (2006).

44. Rezaie, W.L. Headrick, and W.G. Fahrenholtz "Refractory Selection for High Temperature Black Liquor Gasification," Journal of the American Ceramic Society, 89(1) 309-315 (2006).
45. W.G. Fahrenholtz, "The ZrB_2 Volatility Diagram," Journal of the American Ceramic Society, 88(12) 3509-3512 (2005).
46. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Oxidation of ZrB_2-SiC Ceramics Under Atmospheric and Reentry Conditions," Refractories Applications Transactions, 1(2) 1-8 (2005).
47. A.L Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "High Strength ZrB_2-Based Ceramics," Journal of the American Ceramic Society, 87(6) 1170-1172 (2004).
48. A.L. Chamberlain, W.G. Fahrenholtz, G.E. Hilmas, and D.T. Ellerby, "Characterization of Zirconium Diboride Ceramics for Thermal Protections Systems," Key Engineering Materials, 264-268, 493-496 (2004).
49. W.G. Fahrenholtz, G.E. Hilmas, A.L. Chamberlain, and J.W. Zimmermann, "Processing and Characterization of ZrB_2-Based Monolithic and Fibrous Monolithic Ceramics," Journal of Materials Science, 39(19) 5951-5957 (2004). (UMR photo selected for cover of issue)

Theses and Dissertations

The following theses and dissertations have been part of the UHTC research group at Missouri S&T.

1. S. Zhu, "Densification, Microstructure, and Mechanical Properties of Zirconium Diboride Based Ultra-High Temperature Ceramics," PhD dissertation, Missouri University of Science and Technology, 2008.
2. S. Landwehr, "Processing and Characterization of Zirconium Diboride-Molybdenum Cermets," PhD dissertation, Missouri University of Science and Technology, 2008.
3. X. Zhang, "Densification and Mechanical Properties of Tantalum Carbide and Tantalum Diboride Ceramics," PhD Dissertation, Missouri University of Science and Technology, 2008.
4. A. Buchheit, "Improving Thermal Shock Resistance of Silicon Carbide Ceramics," PhD Dissertation, Missouri University of Science and Technology, 2008.
5. M.P. Teague, "Modeling and Measurement of Thermal Residual Stresses and Isotope Effects on Thermo Physical Properties of ZrB_2-SiC Ceramics," M.S. Thesis, Missouri University of Science and Technology, 2008.
6. M.C. Teague, ""Reaction Processing ofUltra-High Temperature W/Ta2C Cermets," M.S. Thesis, Missouri University of Science and Technology, 2008.
7. T. Huang, "Fabrication of Components Using Freeze-Form Extrusion Fabrication," PhD Dissertation, Missouri University of Science and Technology, 2007.
8. J.W. Zimmermann, "Improving the Thermal Shock Resistance of Zirconium Diboride Ceramics," PhD Dissertation, Missouri University of Science and Technology, 2007.
9. A.L. Chamberlain, "Reaction Processing For the Development of Ultra-High Temperature Ceramics," PhD Dissertation, Missouri University of Science and Technology, 2006.

10. A. Rezaie, "Oxidation of ZrB_2-30 vol% SiC at 1500°C With an Emphasis on Reactions Involving SiC," PhD Dissertation, Missouri University of Science and Technology, 2006.

Patent Applications

1. G.E. Hilmas, W.G. Fahrenholtz, and J. Watts, "A Method for Toughening Via the Production of Spiral Architectures Through Powder Loaded Polymeric Extrusion and Toughened Material Formed Thereby," U.S. Provisional Patent Application 60/972,493, filed September 14, 2007.
2. S.C. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Pressurelessly Sintered Zirconium Diboride/Silicon Carbide Bodies and a Method for Producing the Same," application number 11/419,622 filed May 22, 2006.
3. S.C. Zhang, G.E. Hilmas, and W.G. Fahrenholtz, "Reactive Sintering of ZrC/W Composites and Method for Producing the Same," application number 11/539,384 filed October 6, 2006.